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From classical to living/controlled statistical free-radical copolymerization

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Abstract

Solvent effects on monomer reactivity ratio values along with the determination of radical reactivity ratios, their possible origins as well as their importance in conventional free-radical copolymerization is described first. Predictions from data obtained at low conversion of cumulative composition and stereochemical distribution in copolymer chain along with glass transition temperature and the lumped overall copolymerization parameter $\overline{k_p}/\overline{k_t}^{1/2}$ at high conversion are described. Transfer reactions in free-radical copolymerization using classical chain transfer agent as well as the new catalytic chain transfer agent and the effect on the copolymer structure and properties are also studied. Finally the new living/controlled free-radical polymerization process and the preparation of well-controlled statistical copolymers are described to stand out the subtle mechanisms differences between living/controlled and conventional free-radical copolymerization. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Conventional copolymerization; Free radical; Monomer reactivity ratios; Solvent effects; Radical reactivity ratios; Penultimate unit effect; High conversion copolymerization; Chain transfer reactions; Living/controlled free-radical methods; Controlled statistical copolymers

Contents

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1. Introduction

Free-radical copolymerization reactions are important from both practical and theoretical point of view. Theoretically, it is interesting to focus on the effect of the chemical structure on the reactivity of monomers and radicals. Practically, radical copolymerization is the most recommendable process to prepare an unlimited number of polymer compounds by changing the nature and relative proportions of monomers in the reaction medium.

The kinetics and mechanisms involved in the free-radical copolymerization of vinyl monomers have been a research topic of interest for many years. The copolymerization of two monomers, A and B, give rise to the formation of a copolymer chain having composition and sequence distribution, which are dependent on the relative proportion of applied monomers as well as the monomers and radical reactivities. Depending on the species considered different important kinetic models have been developed.

A great impulse of the copolymerization studies emerges from the Symposium on “Free Radical Polymerization: Kinetics and Mechanism” held in Santa Margherite Ligure, Italy, May 1987. Sessions on copolymerization are devoted to point out the importance of the copolymer composition, model discrimination and copolymerization rate.

In the field of free-radical copolymerization, great emphasis has been always put on copolymer composition, appropriately considered as the most important aspect of the polymerization reaction, since it influences the properties of the resultant materials. Then, it is important to estimate the monomer reactivity ratios in a statistical correct manner. O’Driscoll and Reilly [1] based on the Mayo-Lewis Terminal Model (MLTM) analyze different linear and nonlinear regression approaches to estimate the monomer reactivity ratios.

Although the estimation of parameters is important, the copolymer composition is often inadequate to discriminate among models such as MLTM, penultimate unit model (PUM) or complex participation model (CPM). Hill and O’Donnell [2] described a general method based on the nonlinear least-square analysis of copolymer composition or sequence distribution variation with the monomer feed composition. The latter is much more sensitive to probe the mechanism, which best represents a particular copolymerization.

Though before the Santa Margherite Ligure Congress (SMLC) the copolymerization rate had been much less studied, its relevance was well recognized since accurate kinetic modeling, suitable to describe the whole course of the copolymerization reaction, was necessary for any reaction engineering scheme. Russo [3] analyzed the initiation, propagation and termination step in copolymerization. The termination step can be described on the basis of chemical control [4,5], diffusion control [6] and the segmental diffusion model [7]. Furthermore, Russo’s lecture include the first results obtained by Fukuda et al. [8,9] in which the termination step is well fit by chemical or ideal diffusion models and the propagation step does not follow the terminal model, but seems to fulfill the PUM. Furthermore analyzing the propagation step, Russo [3] pointed out that according to literature data the values of monomer reactivity ratios are, in some cases, dependent on the reaction medium. Consequently all the quantities dependent on the reactivity ratios in these cases will also be dependent on the reaction medium, e.g. copolymer composition, average propagation rate constant, etc.

Harwood [10] resolved these apparent anomalies by comparing the copolymer microstructure as a function of copolymer composition instead of comparing the copolymer microstructure as a function of monomer feed composition: the 'bootstrap model' emerged.

Considering that the previous knowledge on copolymerization reaction until 1987 is collected in references and the Lectures of SMLC, this review starts from the data with the new development in conventional copolymerization, such as solvent effects on monomer reactivity ratios, radical reactivity ratios, high conversion reaction and transfer reaction in copolymerization. Furthermore, considering the new living/controlled processes of radical polymerization, which allows preparing polymers with controlled architecture, narrow molecular weight distributions (MWD) and predetermined molecular weights, a general overview on the mechanism and a description of the statistical copolymers obtained from different systems will be also described.

It is also necessary to have in mind the previous and well documented reviews [11–14]. Therefore, the present review does not try to give an exhaustive list of references, but simply to raise a general overview of the current main developments in the statistical free-radical copolymerization.

2. Conventional copolymerization

2.1. General background of the copolymerization mechanisms

Copolymer composition normally differs from monomer feed composition and depends on the values of monomer reactivity ratios.

The first and simplest model, which successfully describes copolymer composition and monomer sequence distribution, is the MLTM [15,16]. This model involves four propagation steps

$$\sim\!\sim\!\mathrm{A}^{\bullet} + \mathrm{A} \xrightarrow{k_{\mathrm{pAA}}} \sim\!\sim\!\mathrm{A}^{\bullet}$$

$$\sim\!\sim\!\mathrm{A}^{\bullet} + \mathrm{B} \xrightarrow{k_{\mathrm{pAB}}} \sim\!\sim\!\mathrm{B}^{\bullet}$$

$$\sim\!\sim\!\mathrm{B}^{\bullet} + \mathrm{A} \xrightarrow{k_{\mathrm{pBA}}} \sim\!\sim\!\mathrm{A}^{\bullet}$$

$$\sim\!\sim\!\mathrm{B}^{\bullet} + \mathrm{B} \xrightarrow{k_{\mathrm{pBB}}} \sim\!\sim\!\mathrm{B}^{\bullet}$$

where $k_{\mathrm{p}ij}$ is the propagation rate coefficient for the reaction of radical i adding monomer j. The ratios of these rate coefficients are the monomer reactivity ratios, $r_i = k_{\mathrm{p}ii}/k_{\mathrm{p}ij}$.

The instantaneous copolymer composition can be written in terms of monomer molar fraction in the copolymer, F_i, and monomer molar fraction in the reaction mixture, f_i:

$$\frac{F_1}{F_2} = \frac{f_1(f_1 r_1 + f_2)}{f_2(f_2 r_2 + f_1)} \tag{1}$$

At least 90% of all known copolymerization systems can be adequately described by the terminal model when copolymer composition versus monomer feed data is concerned [10,11]. However, there are systems that require more complicated models. PUM [17] was developed to introduce the influence on the growing radical reactivity of a monomer unit attached to the terminal unit. Thus radicals AA$^{\bullet}$, BA$^{\bullet}$, BB$^{\bullet}$ and AB$^{\bullet}$ are considered to participate in the process:

$$\sim\!\sim\!\sim \mathrm{AA}^{\bullet} + \mathrm{A} \xrightarrow{k_{\mathrm{pAAA}}} \sim\!\sim\!\sim \mathrm{AAA}^{\bullet}$$

$$\sim\!\sim\!\sim \mathrm{AA}^{\bullet} + \mathrm{B} \xrightarrow{k_{\mathrm{pAAB}}} \sim\!\sim\!\sim \mathrm{AAB}^{\bullet}$$

$$\sim\!\sim\!\sim \mathrm{BA}^{\bullet} + \mathrm{A} \xrightarrow{k_{\mathrm{pBAA}}} \sim\!\sim\!\sim \mathrm{BAA}^{\bullet}$$

$$\sim\!\sim\!\sim \mathrm{BA}^{\bullet} + \mathrm{B} \xrightarrow{k_{\mathrm{pBAB}}} \sim\!\sim\!\sim \mathrm{BAB}^{\bullet}$$

$$\sim\!\sim\!\sim \mathrm{AB}^{\bullet} + \mathrm{A} \xrightarrow{k_{\mathrm{pABA}}} \sim\!\sim\!\sim \mathrm{ABA}^{\bullet}$$

$$\sim\!\sim\!\sim \mathrm{AB}^{\bullet} + \mathrm{B} \xrightarrow{k_{\mathrm{pABB}}} \sim\!\sim\!\sim \mathrm{ABB}^{\bullet}$$

$$\sim\!\sim\!\sim \mathrm{BB}^{\bullet} + \mathrm{A} \xrightarrow{k_{\mathrm{pBBA}}} \sim\!\sim\!\sim \mathrm{BBA}^{\bullet}$$

$$\sim\!\sim\!\sim \mathrm{BB}^{\bullet} + \mathrm{B} \xrightarrow{k_{\mathrm{pBBB}}} \sim\!\sim\!\sim \mathrm{BBB}^{\bullet}$$

To calculate the copolymer composition using the penultimate model four monomer reactivity ratios are necessary ($r_i = k_{\mathrm{p}iii}/k_{\mathrm{p}iij}$ and $r_i' = k_{\mathrm{p}jii}/k_{\mathrm{p}jij}$) where $k_{\mathrm{p}ijm}$ is the rate coefficient for the addition reaction of monomer m to the ij radical, where i, j, m are A and/or B.

The resulting copolymer composition equation is:

$$\frac{F_1}{F_2} = \frac{1 + \dfrac{r_{BA}x(r_{AA}+1)}{r_{BA}x+1}}{1 + \dfrac{r_{AB}(r_{BB}+x)}{x(r_{AB}+x)}} \tag{2}$$

where $x = f_1/f_2$.

Besides MLTM and PUM, the CPM [18,19] and depropagation model (DPM) [20,21] have been described. In the CPM, monomers form complexes and these complexes participate in the propagation reaction. In the case that monomers are applied that can undergo depropagation, the DPM has to be used, e.g. α-methyl styrene.

2.2. Monomer reactivity ratios: solvent effects

For many years it was believed that monomer reactivity ratios are insensitive to the solvent employed in the copolymerization. However, increasing experimental data emerged in which it became apparent that this insensitiveness appears not to be true. A pronounced effect of the reaction medium was found for the systems consisting of, at least, one polar monomer. In fact, a solvent effect has been described for systems involving monomers such as acrylic acid or methacrylic acid, which can associate in solution [22]. The monomer reactivity ratios of these monomers, when copolymerized with other monomers, appeared to change dramatically with the nature of the solvent. The reactivity ratios of acrylic acid (AA) or methacrylic acid (MAA) are higher in nonpolar solvents (e.g. C_6H_6 or CCl_4) than in polar solvents (e.g. DMF) [23–30]. The subject has been reviewed by Plochocka [31].

Besides the effects of the reaction medium on the copolymerization of the monomers capable of ionization or H-bond formation, an effect of solvents upon copolymerization of apparently neutral monomers has also been found.

Ito and Otsu [32] in 1969 were probably the first who described the effect of benzene, benzonitrile, benzyl alcohol, and phenol on the free-radical copolymerization of styrene (S) with methyl methacrylate (MMA). Later many reports about solvent effect on copolymerization have been published. In general, small effects of solvents on copolymerization reactivity ratios have been observed: their extents have been strongly dependent on the monomer nature and the solvents involved. First attempts to explain this behavior were based on the polarity of solvents. Thus, Ito and Otsu [32] indicate that the observed variations of the reactivity ratios in S–MMA copolymerization were due to the polarized structure of MMA in the transition state, which becomes more important when the solvent polarity increases. Other studies have shown linear dependencies between copolymerization parameters and the dielectric constant in the copolymerization of S with methacrylonitrile (MAN) [33] or in the copolymerization of S with MMA [34,35]. The observed results were explained on the basis of the polarized forms by the electron-donating or the electron-withdrawing character of their functional groups.

However, this effect may be only apparent, since, the polarity effect, as well as other mechanisms has also been proposed to describe the effect of solvents. Monomer–monomer, monomer–solvent, or radical–solvent (which may not only be solvent, but also one or both comonomers) complexes and the so-called bootstrap model can also explain the apparent variation of copolymerization parameters in different solvents [36]. To date there is experimental evidence [36] that the bootstrap model is the most appealing as a general model. This model was proposed by Harwood [10] who observed that copolymers with the same composition have the same microstructure independent of the solvent used during their preparation. Therefore, the conditional probabilities governing sequence distribution are unaffected by the polymerization medium and consequently, the monomer reactivity ratios are not affected either.

In the copolymerization of an A–B system, the conditional probability, $P(\mathrm{A/B})$ that an A unit follows a B unit is given by [37]

$$P(\mathrm{A/B}) = \frac{1}{1 + r_{\mathrm{B}}([\mathrm{B}]/[\mathrm{A}])} \tag{3}$$

but as Harwood recognized [10], [B]/[A] is the ratio of monomers in the vicinity of the growing radicals, which need not be equal to the ratio of monomers charged in the polymerization systems, $[\mathrm{B}^0]/[\mathrm{A}^0]$, since an equilibrium may exist in which monomers are distributed between the free solvent and the surrounding of growing radicals.

Harwood [10] has indicated that $P(\mathrm{A/B})$ may be appropriated to the following expression:

$$P(\mathrm{A/B}) = \frac{1}{1 + r_{\mathrm{B}}K([\mathrm{B}^0]/[\mathrm{A}^0])} \tag{4}$$

where

$$K = \frac{[\mathrm{A}^0][\mathrm{B}]}{[\mathrm{B}^0][\mathrm{A}]} \tag{5}$$

is the partition coefficient that characterizes the distribution of monomers in the system.

Taking this fact into account, Harwood [10] has suggested that solvent effects in copolymerization are not manifested in the chain end reactivity but rather in a solvent partitioning whereby an equilibrium may exist in which monomers are distributed between the free solvent and the domains of growing polymer radicals.

Harwood, in his original paper, analyzes four systems: styrene–methacrylic acid, styrene–acrylic acid, styrene–acrylamide and vinylidene chloride–methacrylonitrile. In all of them, the monomer reactivity ratios vary considerably as the reaction solvent is varied but the copolymers that are produced have the same microstructure when they have the same copolymer composition.

Further confirmation were made by Park et al. [38] by cycling pairs of acrylamide unit in copolymers to imide unit, and Davis [39] who re-examined the microstructure data previously published for styrene (S)–methyl methacrylate (MMA) [40,41] and claimed that the bootstrap model is operative in the copolymerization of S–MMA in benzene, chlorobenzene and benzonitrile. Other papers fully confirmed and provide new evidences about this phenomena [42–44].

An important advance in the solvent effects on the copolymerization parameters was the attempt to quantify the partition coefficient. Klumperman and O'Driscoll [45] chose the bulk copolymerization as a thermodynamic reference state and assessed the partition coefficient in bulk as unity. They assume that the ratio of the monomers in the feed is the same in the vicinity of the growing chain radical and in the whole system when the copolymerization is performed in bulk.

Considering r_i^{b} as the monomer reactivity ratios in bulk and r_i^{s} as the apparent monomer reactivity in a given solvent, and taking into account Eqs. (3) and (4), r_i^{s} can be expressed as

$$r_i^{\mathrm{s}} = K r_i^{\mathrm{b}} \tag{6}$$

where K is the partition coefficient

$$K = \frac{r_i^{\mathrm{s}}}{r_i^{\mathrm{b}}} \tag{7}$$

Considering [37]

$$P(\mathrm{A}/\mathrm{B}) + P(\mathrm{B}/\mathrm{A}) = 1 \tag{8}$$

it is easy to deduce that

$$r_{\mathrm{A}}^{\mathrm{s}}.r_{\mathrm{B}}^{\mathrm{s}} = r_{\mathrm{A}}^{\mathrm{b}}.r_{\mathrm{B}}^{\mathrm{b}} \tag{9}$$

Furthermore, analyzing the copolymer composition and the microstructure as a function of the relevant conditional probabilities [37] the following equation can be obtained:

$$P(\mathrm{A}/\mathrm{B}) = P(\mathrm{B}/\mathrm{A}) = \frac{1 - \sqrt{4F_{\mathrm{A}}^2(1 - r_{\mathrm{A}}r_{\mathrm{B}}) - 4F_{\mathrm{A}}(1 - r_{\mathrm{A}}r_{\mathrm{B}}) + 1}}{2F_{\mathrm{A}}(1 - r_{\mathrm{A}}r_{\mathrm{B}})} \tag{10}$$

which implies that, given the bootstrap model's correctness, the monomer reactivity ratio product should be constant even when the individual monomer reactivity ratios change from solvent to solvent. Apparent values of monomer reactivity for styrene–methyl methacrylate system in various solvent [34, 35] have shown that $r_{\mathrm{A}}r_{\mathrm{B}}$ does not vary from solvent to solvent. However, in other systems, such as, methyl methacrylate–butyl acrylate, the partition coefficient values depend on the monomer reactivity ratio from which K is determined [46]. Klumperman and Kraeger [47] have described a similar trend for the styrene–acrylonitrile system copolymerized in toluene, 2-butanone and *N*,*N*-dimethylformamide. In order to explain this feature, Klumperman and Kraeger [47] stated that, considering the bootstrap effect as a consequence of the differences in polarity between solvent and polymer phase, the partition coefficient might be linearly dependent on copolymer composition. However, though Klumperman and Vonk [48] observed a qualitative bootstrap effect on the copolymerization of styrene with maleic anhydride, they cannot interpret the solvent effect quantitatively.

Furthermore, Maxwell et al. [49] considered that a 'template' effect or 'solvent–polymer complex' effect is a second possibility by which the local monomer concentration at the polymerization site may differ from that in the bulk phase. They suggested that there are no reasons to believe that the bootstrap effect is constant for various monomer ratios. Therefore, the composition dependence on the partition coefficient can be described by an empirical equation:

$$K = \frac{([\mathrm{A}]/[\mathrm{B}])^z}{[\mathrm{A}^0]/[\mathrm{B}^0]} \tag{11}$$

in which, by suitable adjustment, the reactivity ratios and the empirical parameter z are able to fit the experimental data of overall propagation copolymerization coefficient. However, the results are unrealistic since the calculated reactivity ratios would not properly predict the sequence distribution.

In order to estimate qualitatively which monomer is preferentially sorbed, Madruga and Fernández-García considered [46] a value of unity for the partition coefficient in the bulk system. They assumed that the cause of the solvent effect on the reactivity ratios is mainly due to differences between the local and analytical monomer ratios. Then, a mole fraction in the copolymer chain F_A is considered, and from the copolymer composition equation and the apparent reactivity ratios, the analytical bulk (f_A^b) and the analytical solution (f_A^s) monomer feed compositions are determined. Differences between analytical bulk and solution monomer feed composition as a function of copolymer chain composition give us an indication of the monomer preferentially sorbed. From this procedure it has been observed that the enrichment or the depletion of a determined monomer around the growing radical is dependent on both the copolymer composition and the solvent in which the copolymerization is performed. Copolymer composition determines the amount of monomer that is preferentially sorbed around the growth chain radical whereas polarity of the solvent determines what monomer is preferentially sorbed [46]. In this way two different trend were observed when S–MMA and styrene (S)–butyl acrylate (BA) systems [50] are performed in benzene (dipole moment 0.3 D) or benzonitrile (dipole moment 3.57 D). When benzonitrile is used as a solvent the vicinity of the growing radicals became relatively rich in MMA or BA. Futhermore for the S–BA system a higher amount of acrylic monomer is surrounding the growing radicals. This could be explained considering the polarity of the reaction medium. If it is assumed that the polarity of the reaction medium is a function of each component's polarity and its corresponding molar fraction, S–BA will have a slightly higher polarity than S–MMA, since the dipole moments have values of 1.67 and 1.93 D for MMA and BA, respectively. However, when benzene is used to perform the copolymerization, this does not have a significant influence for the S–BA system, but in the case of S–MMA copolymerization, styrene is the monomer preferentially sorbed around the growing radical.

The influence of the polarity of the reaction medium has been put forward since the first papers about the effect of solvent on copolymerization parameters were published. Equivalent observations to that of S–BA and S–MMA systems have also been made for methyl methacrylate–butyl acrylate copolymers performed in benzene or benzonitrile solutions [51]. Moreover, the effect of solvent polarity on the local monomer concentration is noted when 2-hydroxyethyl methacrylate (HEMA) is copolymerized with styrene in solvents with a low dipole moment (toluene) or with a high dipole moment (*N*,*N*′-dimethylformamide) [52,53].

It is well known that the degree of association in monomers such as HEMA is important hence, the sensitivity of the monomer reactivity ratios to the solvent in which the polymerization is performed has been mainly attributed to the different tendency of such monomers to form aggregates. Despite these facts, a bootstrap effect has also been claimed to explain the solvent effects on the apparent variation of monomer reactivity ratios on the free-radical copolymerization of HEMA–dodecyl methacrylate [54], HEMA–styrene [52,53] or HEMA–butyl methacrylate [55,56]. From preferential adsorption measurements the bootstrap model has been also utilized to explain the solvent effects on free-radical copolymerization of 2-ethyl acrylic acid–methacrylic acid [57] and those of the 2-hydroxyethyl acrylate with itaconic acid [58].

However, not only the polarity of solvents plays a role but also the differences between the local monomer concentration at the polymerization site and the monomer concentration in the bulk phase may arise, if the solvent in which the copolymerization is performed avoids the selective association of HEMA with the growing copolymer chain. In this way the bootstrap effect is operative for HEMA–*t*-butyl acrylate (*t*BA) system when the solvents used are 1,4-dioxane (dipole moment 0.0 D) and *N*,*N*-dimethylformamide (dipole moment 3.7 D) [59]. In both cases an apparent enrichment of *t*BA monomer at the polymerization site is observed [59]. However, this fact means that when the copolymerization is carried out in bulk, the HEMA associates strongly with the poorly solvated polymer chain, whereas the addition of 1,4-dioxane or DMF to the reaction medium produces a more effective chain solvation avoiding its selective association with HEMA. As a consequence the HEMA local concentration around the growing radical diminishes and the enrichment of *t*BA monomer at the site of polymerization is only apparent [59].

Semchikov et al. [60,61] observed that copolymer chain composition is, in many cases but not always, a function of chain length. The fact that the composition depends on molecular weight is explained by preferential sorption of one of the monomers by polymer chains, resulting in the preferential composition coefficient dependent upon the length of the growing chain [60,62]. Semchikov [63] concludes that specific thermodynamic properties of monomer mixtures as a solvent for copolymers lead to preferential sorption of one of the monomers by the polymer coils and preferential solvation of growing chains. Subsequently, Kuchanov and Russo [64] develop a theoretical approach based on thermodynamic considerations. From monomer reactivity ratio, initial monomer feed and the parameter of pair interactions between monomer units, monomers and solvent molecules, Kuchanov and Russo [64] derive an equation for finding the equilibrium dependence of the monomer mixture composition inside the growing copolymer chain.

Besides the bootstrap effects, solvents may affect the propagation step in free-radical copolymerization in a number of different ways. Several possibilities have been reviewed by Coote et al. [36].

A polar effect of solvent is operative when the solvent affects the reactivity of the different types of propagation steps without directly participating in the reaction. The polarity effect might be only significant when the considered copolymerization system involves strongly electrophilic and nucleophilic monomer pairs and the charge transfer stabilization of the transition state would occur to different extents in the cross- and homopropagation reactions [36].

Monomer–monomer complexes may also interfere with the propagation step since complexation might stabilize the monomer, alter its steric properties and/or provide an alternative pathway for propagation. Furthermore, monomer–monomer complexes may propagate as a single unit, but suffer dissociation during propagation otherwise is simple to alter the monomer concentration [36]. The participation of monomer–monomer complex on the propagation step has been introduced to modify the MLTM by Seiner and Litt [18] and Cais et al. [19]. When monomer–monomer complexes do not propagate, similar results to the bootstrap effect may be produced [36].

Solvents (where solvent can also be a comonomer) may also affect the propagation step via formation of radical–solvent complexes. Given the experimental evidence for the existence of radical–solvent complexes [65,66] and their influence on the free-radical homopolymerization [66–68] many workers have invoked this model to explain the solvent effects on copolymerization [34,35]. Recently, O'Driscoll et al. [69] suggest that the effect of benzyl alcohol on the apparent propagation rate coefficient for homopolymerization of methyl methacrylate (MMA) and styrene (S) and on S–MMA copolymerization (S/MMA = 1:1) can be described by radical–solvent complexes. However, when radical–solvent or radical–monomer complexes do not propagate, the effect of complexation is to alter the effective radical or monomer concentrations, thereby causing a bootstrap effect [36].

In summary, the bootstrap model establishes the most general qualitative interpretation of solvent effect on free-radical copolymerization. However, the subtle specific effect of solvents on the propagation step may be not only preferential solvation of the entire chain, but also preferential solvation of chain end, radical–solvent or momomer–solvent complex as well as nonreactive monomer–monomer complexes may be the cause of the bootstrap phenomena.

2.3. Radical reactivity ratios: penultimate unit effect

From many years MLTM have been widely accepted as the basis of copolymerization kinetics. Considering its success to predict the composition of copolymers from a given monomer feed composition, the average propagation rate coefficient in copolymerization, $\overline{k_\mathrm{p}}$, would be predicted as follows [70]

$$\overline{k_\mathrm{p}} = \frac{r_\mathrm{A} f_\mathrm{A}^2 + 2 f_\mathrm{A} f_\mathrm{B} + r_\mathrm{B} f_\mathrm{B}^2}{[r_\mathrm{A} f_\mathrm{A}/k_{p\mathrm{AA}}] + [r_\mathrm{B} f_\mathrm{B}/k_{p\mathrm{BB}}]} \tag{12}$$

and the average copolymerization rate can only be predicted under assumption of models for the termination copolymerization step: The first model was the chemical control model [4,5] described for the so-called ϕ factor defined as

$$\phi = \frac{k_{t\mathrm{AB}}}{(k_{t\mathrm{AA}} k_{t\mathrm{BB}})^{1/2}} \tag{13}$$

where $k_{t\mathrm{AA}}$, $k_{t\mathrm{BB}}$ and $k_{t\mathrm{AB}}$ are the homotermination and the crosstermination, respectively.

The strong dependence of ϕ factor values on the monomer feed composition and the evidence for diffusion control in the termination process led North et al. [6,71] to propose the diffusion control model. According to Atherton and North [6,71], at least at low conversion the average termination copolymerization coefficient is governed by segmental diffusion. In the 'ideal' case it can be assumed that average termination coefficient is a linear function of copolymer composition

$$k_\mathrm{t} = F_\mathrm{A} k_{t\mathrm{AA}} + F_\mathrm{B} k_{t\mathrm{BB}} \tag{14}$$

where F_i is the molar fraction of monomer i on the copolymer chain.

Finally, Russo and Munari [7] proposed a model, which includes physical, and chemical parameters, which can control the bimolecular termination kinetics.

In 1985 Fukuda et al. [8,9] measured the average propagation and the average termination rate coefficients in methyl methacrylate–styrene and in *p*-chlorostyrene–butyl acrylate copolymerization systems. They found that the experimental average propagation rate coefficient does not follow the terminal model and the experimental average termination rate coefficient can be adequately described by the chemical control model proposed by Walling [5] with $\phi = 1$, as well as the 'ideal' diffusion control model proposed by Atherton and North [6].

In subsequent studies, for a number of copolymerization systems and using the new pulsed laser polymerization method (PLP) [72], Olaj et al. [73,74] and O'Driscoll et al. [75–77] measured $\overline{k_\mathrm{p}}$ and observed a general behavior similar to that described by Fukuda et al. [8,9].

The failure of the terminal model to describe average propagation rate constants in free-radical copolymerization would indicate that the copolymerization termination models previously considered might have no physical meaning. Therefore, the various constants or pseudo-constants which described the referred termination step model can only be considered as adjustable parameters to fit the experimental results with the proposed equations.

In order to explain the experimental variation of average propagation coefficient as a function of monomer feed composition in copolymerization, Fukuda et al. [8] postulated a penultimate unit effect

(PUE) in the propagation rate coefficient. Therefore $\overline{k_p}$ may be expressed as

$$\overline{k_p} = \frac{\overline{r_A} f_A^2 + 2 f_A f_B + \overline{r_B} f_B^2}{\dfrac{\overline{r_A} f_A}{\overline{k_{pAA}}} + \dfrac{\overline{r_B} f_B}{\overline{k_{pBB}}}} \tag{15}$$

where

$$\overline{r_A} = \frac{r_{BA}[f_A r_{AA} + f_B]}{f_A r_{BA} + f_B}, \qquad \overline{r_B} = \frac{r_{AB}[f_B r_{BB} + f_A]}{f_B r_{AB} + f_A} \tag{16}$$

and

$$\overline{k_{pAA}} = \frac{k_{pAAA}[r_{AA} f_A + f_B]}{r_{AA} f_A + \dfrac{f_B}{s_A}}, \qquad \overline{k_{pBB}} = \frac{k_{pBBB}[r_{BB} f_B + f_A]}{r_{BB} f_B + \dfrac{f_A}{s_B}} \tag{17}$$

where s_A and s_B are the radical reactivity ratios defined by

$$s_i = \frac{k_{pjii}}{k_{piii}} \tag{18}$$

and k_{pijm} are the propagation rate constants, with i, j and m representing the penultimate, the terminal and monomer unit, respectively.

The first model proposed by Fukuda et al. [8,9] assumes that the MLTM reactivity ratios, r_A and r_B, are not affected by the penultimate units since the terminal model could be fitted to the composition data and consequently, only if s_A and s_B deviate from the unity, the penultimate unit of the chain is having a kinetic effect on the reaction. This model is called implicit penultimate unit model (IPUM), to differentiate from the explicit penultimate unit model (EPUM) in which, the PUE are significant in both monomer and radical reactivity ratios [78].

A number of systems, collected in previous published rewievs [79–81] have been so far tested and, in a general context, most of then shown that the composition data could be fitted by the MLTM, but propagation rate coefficients need to use the radical reactivity ratios. Systems such as those formed by styrene–meth(acrylic) monomers as well as those formed by styrene or methacrylic monomers with diitaconates, fumarates or maleimides are in agreement with the IPUM.

However, the terminal model can adequately describe both the composition and kinetic behavior of monomer pairs with sterically similar structure. Then *p*-methoxystyrene–styrene [82], methyl methacrylate–dodecyl methacrylate [83], methyl methacrylate–butyl methacrylate [83] or *p*-chlorostyrene–*p*-methoxystyrene [84] systems are well fitted by the MLTM. However, there are other systems in which the MLTM cannot describe the copolymerization behavior of monomers with similar structure, such as *p*-chlorostyrene–styrene [84] system.

A similar, but less direct test of the PUE can be done using standard techniques to measure steady-state polymerization rates. In this analysis [80,85] instead of the propagation rate constant, the parameter $w = \overline{k_p}/\overline{k_t^{1/2}}$ is used, where $\overline{k_p}$ and $\overline{k_t}$ are the average, composition dependent, copolymerization propagation and termination rate constants, respectively. Following the Fukuda et al. [80,85] treatment and under the assumption that termination of copolymerization can be expressed by the chemical factor $\phi = 1$, the penultimate model expression for $w = \overline{k_p}/\overline{k_t^{1/2}}$ reads as:

$$w = \frac{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}{\left(\dfrac{r_1 f_1}{w_1}\right) + \left(\dfrac{r_2 f_2}{w_2}\right)} \tag{19}$$

where

$$\overline{w_i} = \frac{w_i(r_i f_i + f_j)}{r_i f_i + s_i^{-1}} \qquad (i \neq j) \tag{20}$$

being $w_i = k_{\mathrm{p}iii}/k_{\mathrm{t}}^{1/2}$ and r_i and s_i the monomer and radical reactivity ratios.

Although the determination of radical reactivity ratios from this method is performed through free-radical conventional techniques and the measurements are carried out in similar experimental conditions to that used in commercial polymer preparation, it would be emphasized that the use of Eq. (19) to determine radical reactivity ratios have an important constraint: it must be assumed that the overall copolymerization termination rate follows the chemical model [5] with $\phi = 1$.

This restricted model has been analyzed by Fukuda et al. [85] using the literature data and assuming that $s_{\mathrm{A}} = s_{\mathrm{B}}$. A agreement with experimental data is found.

Measurement of radical reactivity ratios using Eq. (19) has been carried out for a number of systems [46,86–89] but instead the use of a single value for both radical reactivity ratios, two different values were used.

Considering the error inherent in the experimental procedures Coote et al. [90] and Heuts et al. [91] have pointed out that the radical reactivity ratios are extremely sensitive to small changes in both, the copolymerization and homopolymerization rate coefficients, as well as the monomer reactivity ratios used in their determination. In this way, several authors [8,73,75] have found different values for radical reactivity ratios in styrene–methyl methacrylate copolymerization. Recently Coote et al. [90,92] have studied the radical reactivity ratios for this system in a large range of temperatures. They have found that the extreme sensitivity of the estimated parameters to small uncertainties in the data prevented the accurate and precise estimation of the individual radical reactivity ratios.

On the other hand, copolymerization systems consisting of monomer pairs where one of the two monomers is varied within a specific family, e.g. styrene (A)–alkyl acrylates (B), have different behavior and consequently different values in radical reactivity ratios. Experimental works indicate that radical reactivity ratios have similar values for styrene–methyl acrylate and styrene–butyl acrylate systems but markedly different for styrene–ethyl acrylate system. For styrene–methyl acrylate and styrene–butyl acrylate systems Davis et al. [77] and for styrene–butyl acrylate system Fernández-García et al. [89] have found that when penultimate unit is an acrylate there is no effect on propagation rate whereas a fairly strong effect was observed when styrene is the penultimate unit. However, Ma et al. [93] show that in the styrene (A)–ethyl acrylate (B) system, only s_{A} can be determined while s_{B} remains unknown. Differences can arise as a consequence of not only the uncertainty of the reported values in alkyl acrylate homopropagation coefficients, but also because $r_{\mathrm{B}}/k_{p\mathrm{BBB}}$ is smaller than $r_{\mathrm{A}}/k_{p\mathrm{AAA}}$ by two orders of magnitude. Furthermore Ma et al. [93] have observed that although the termination step in *p*-chlorostyrene–methyl acrylate system is well described by the chemically controlled model [9], the termination step in the styrene–ethyl acrylate system does not conform neither the chemically controlled model [5] nor the North ideal diffusion model [6], but a model in which the termination step is controlled by purely diffusion motion of the two radicals [81,93,94].

In a very recent paper, Davis [95] has described that subtle variations in monomer structure can have a strong effect on monomer reactivity ratio values. Thus, in the copolymerization of styrene with three structurally related monomers: methyl methacrylate, methyl ethacrylate and dimethyl itaconate, the propagation behavior is different. For styrene–methyl ethacrylate, the terminal model can describe the copolymerization, whereas for styrene–methyl methacrylate or styrene–dimethyl itaconate $\overline{k_{\mathrm{p}}}$ has values, which are, respectively, lower or higher than the terminal model predictions. Davis [95] concludes that α substitution plays a significant role in determining the influence of terminal and penultimate units on the propagation rate. Differences on the radical reactivity ratios are also noted in the methyl methacrylate (A)–dimethyl itaconate (B) [86] or methyl methacrylate (A)–dibutyl itaconate (B) [87] systems. The radical reactivity ratio values for both itaconates indicate that when the penultimate unit is A both itaconate derivatives have a similar effect on the propagation rate. However, when the penultimate unit is dibutyl itaconate, the growing radical seems to be more reactive towards methyl methacrylate monomer than when penultimate unit is methyl methacrylate, whereas in the case of dimethyl itaconate the reverse might be true. However, for the copolymerization of methyl methacrylate–methyl acrylate [88] or methyl methacrylate–butyl acrylate [46] systems a similar effect in PUE on copolymerization behavior has been observed. Considering that diitaconate systems have different substituents on the α position whereas the mentioned alkyl acrylates do not have α substituents, it seems again that the α-substituent might affect the propagation rate coefficients. However, it has been stated [96] that the copolymerization propagation rate coefficient measured by PLP technique at 40 °C and 1000 bar for dodecyl methacrylate (DMA)–methyl acrylate (MA) and methyl methacrylate (MMA)–butyl acrylate (BA) systems satisfactorily fits the implicit penultimate unit effect (IPUE) model, neither the IPUE nor the explicit penultimate unit effect (EPUE) model are capable of simultaneously fitting the rate and composition data for DMA–dodecyl acrylate (DA) and MMA–DA. At this point it is remarkable to point out that for methyl methacrylate systems the results obtained from PLP measurements of $\overline{k_p}$ [97] are in good agreement with those obtained from w measurements [46]. Taking into account the uncertainty of the radical reactivity ratio values, the IPUM cannot be critically tested by merely examining its fit to a set of data. Consequently, the obtained results have to be compared with the suggested theoretical predictions.

As a theoretical justification of the implicit penultimate model Fukuda et al. [98] proposed the stabilization energy model in which it is suggested that the penultimate unit affect only the stability of the reacting radical and thus the reaction enthalpy. However, the penultimate unit is far away to interact with the reacting monomer. Therefore, the rate at which a radical propagates is determined by the reactivity of the terminal radical mediated by the penultimate unit. Fukuda et al. [85,98] have also assumed that there are no penultimate effects in the frequency factor and that the Evans-Polanyi [99,100] rule is valid. Fukuda et al. [98] conclude that the relationship between the monomers and radical reactivity ratios is given by

$$r_1 r_2 = s_1 s_2 \tag{21}$$

In order to test the validity of this conclusion, O'Driscoll [79] has plotted values of $s_1 s_2$ against values of $r_1 r_2$. For most of the considered copolymerization systems, he has found a good correlation between these two products. Later, Fukuda et al. [80,81] introduced new monomer pairs in a similar plot and also found that most of the data are scattered around the plot diagonal. Therefore, most of the literature data suggest that the correlation between $s_1 s_2$ and $r_1 r_2$ might be real.

The experimental results of copolymerization rate for methyl methacrylate–methyl acrylate [88], methyl methacrylate–butyl acrylate [46], methyl methacrylate–dimethyl itaconate [86] or methyl methacrylate–dibutyl itaconate [87] measured in steady-state are also in agreement with the theoretical ones using radical reactivity ratios whose values are given by $s_A = r_A r_B / s_B$.

However, there are systems in which large differences exist between these products. Coote et al. [84] in the copolymerization of *p*-chlorostyrene–styrene and *p*-chlorosyrene–*p*-methoxystyrene found significant differences between the product s_1s_2 and r_1r_2. Under the constraint that $r_1r_2 = s_1s_2$ it was impossible to achieve an adequate simultaneous fit of the implicit penultimate model to copolymer composition data and propagation rate coefficients.

Besides there are other systems that also fail to fit Fukuda's predictions. In the copolymerization of methyl methacrylate–ethyl α-benzoyloxymethyl acrylate in benzene [101] the product of monomer reactivity ratios differs from unity, but the variation of the w parameter with monomer feed composition can only be described when both radical reactivity ratios are equal to one. Furthermore, in styrene–butyl acrylate [89] system the correlation between product r_1r_2 (0.163) and s_1s_2 (0.010) predicted in the phenomenological model of Fukuda et al. [98] via radical stabilization energy does not exactly hold.

Heuts et al. [102], considering that a steric interaction may be, at least, equally important in the PUE as the electronic interaction, have introduced the entropic model. In this model [102], it is suggested that among the factors that govern propagation rate coefficient, the Arrhenius frequency factor causes the main difference between different monomers. A very important contribution to the Arrhenius frequency factor is made by certain internal motions hindered in the transition state of the reaction in such a way that the size of the substituent determines the internal barriers (i.e. degree of hindrance) to these motions; greater the hindrance, smaller the Arrhenius frequency factor is. Then, an increase of the rotation barrier decreases the rotational partition function and hence, decreases the frequency factor.

It is evident from the above concern that replacing the substituent of the penultimate unit by another substituent can change the hindrance to the important motions. Hence, they conclude in general that

$$A_{iim} \neq A_{jim} \tag{22}$$

where A_{xym} ($x, y, m = i$ or j) is the frequency factor of the propagation rate coefficient on the addition of a monomer m to a radical y and penultimate unit x.

Radical reactivity ratio s_i can be approximated by

$$s_i \approx \frac{A_{jii}}{A_{iii}} \tag{23}$$

which means that $k_{\mathrm{p}xym} \approx A_{xym}$.

When the implicit penultimate model is considered, the terminal model can adequately fit the copolymer composition, which means that

$$r_i' \approx r_i'' \approx r_i \tag{24}$$

consequently

$$\frac{A_{iii}}{A_{iij}} \approx \frac{A_{jii}}{A_{jij}} \approx \frac{A_{ii}}{A_{ij}} \tag{25}$$

The effect of the hindrance of the penultimate unit may cancel out if the two comonomers are not too dissimilar in size, since both numerator and denominator involve the same penultimate unit. However, the explicit penultimate effect may be effective if the two comonomers are very different in size.

For styrene–butyl acrylate system [89] a semiquantitative evaluation of the different rotational barrier of the terminal C–C bond seems to qualitatively explain that the radical reactivity ratios may result from a steric contribution.

The determination of radical reactivity ratios for pairs of monomers, which contains a monomer with a low ceiling temperature, such as styrene–α-methyl styrene [103] or styrene–methyl ethacrylate [104] indicates that entropic factors play an important role in the copolymerization. Then the diminishment of $\overline{k_p}$ with decreasing molar fraction of styrene in the feed has been attributed to an entropic factor associated with the α-methyl group in α-methyl styrene. In a similar way, the bulky methyl ethacrylate radical plays a significant role in the magnitude of $\overline{k_p}$. The entropic factor is also claimed for the $\overline{k_p}$ values for the styrene (S)–dimethyl itaconate (DMI) system, which are substantially above that the ones predicted by the terminal or the implicit penultimate models [105], the discrepancy being largest for high feed concentration of DMI. A strong entropic effect on DMI propagation has been suggested since when the DMI penultimate unit is replaced by a monomer with less bulky sustituents (e.g. styrene) the DMI propagation proceeds much faster.

On the other hand Coote et al. [90,92] have performed PLP experiments of styrene–methyl methacrylate in a wide range of temperatures. The extreme sensitivity of the radical reactivity ratios to small errors on the kinetic data make it difficult to determine whether the individual parameters are temperature dependent. However, a temperature effect over the average radical reactivity ratios ($s = s_A = s_B$) seems to appear, which suggests that there may be an enthalpic component.

As mentioned above the copolymerization of *p*-chlorostyrene with *p*-methoxystyrene or *p*-chlorostyrene with styrene [84] indicates that $r_1 r_2 \neq s_1 s_2$ and this behavior is attributed to a polar effect in the transition state of the radical addition reaction. This assumption is based on theoretical studies of the transition structure in free-radical addition reactions for methyl radicals to substituted alkenes. These indicate that the Evans-Polanyi rule [99,100] will break down if the transition state is stabilized by polar interaction as occurs when one of the coreactants is electrophilic and the other is nucleophilic [106]. Considering that in Fukuda's model the Evans-Polanyi rule is considered to be valid for the propagation reaction, the failure on the equality proposed by Fukuda's model has been attributed to polar interactions on the cross-propagation reactions of free-radical copolymerization [84].

In addition, Giese et al. [107] have studied the effect of β and γ substituents on the selectivity of an alkyl radical in the addition reaction with alkenes proposing a polar origin for the PUE.

Furthermore, studies of small-radical addition reactions have shown that the γ-substituent (penultimate unit) [108–110] can affect the stability of the charge transfer configurations of the transition structure, and this causes an explicit effect in the barrier. This direct evidence for EPUEs has been attributed to a polar origin and to date is limited to systems involving polar substituents, such as nitrile groups.

Based on the previous results, the so-called Polar Model [107,108] was proposed in which the penultimate unit stabilizes the charge transfer configuration of the transition state, resulting in an EPUE in the barrier.

In a recent review Coote and Davis [111] summarize all the experimental and theoretical results that can influence the effect of penultimate and terminal units on the propagation kinetics. The analysis of the possible factors indicate that polar interactions, radical stabilization effects, direct interaction and entropic effects may be important in the propagation step in copolymerization.

The reviewed studies indicate that, except for a few systems, the terminal model cannot explain the variation of $\overline{k_p}$ as a function of the molar fraction in the monomer feed. The IPUM can be used to describe the behavior of many copolymerization systems. However, the simple assumptions underpinning the model are open to question as enthalpic, entropic and polar effect have been demostrated to play a significant roles. Therefore the implicit model, though based on a simplification of the overall copolymerization mechanism can sometimes be justified as a pragmatic model use for descriptive purposes.

2.4. Free-radical copolymerization at high conversion: predictions of high conversion parameters from data obtained at low conversion

A typical free-radical copolymerization shows a gradual drift in copolymer composition over the course of copolymerization. The copolymer composition drift stems from the different monomer reactivities towards the growing polymer radicals. Hence, the most reactive comonomer is depleted faster than the other comonomer, causing the product to become gradually enriched in the less reactive comonomer as the reaction progresses. Thus, the final polymer material is a combination of many individual copolymer chains with compositions, microstructures and properties that differ from each other. The effect of conversion on the instantaneous comonomer feed composition and therefore, on the polymer composition and sequence distribution, is of considerable interest since copolymers of technical importance are normally obtained at high degrees of monomer conversion. Thus, the composition and sequence distribution of a copolymer varies with conversion, and the extent of this variation depends on the mechanism and reactivity ratios of the copolymerization reactions. Furthermore, polymer properties are controlled by molecular properties such as molecular weight, MWD, chemical composition and stereochemical sequences of copolymer chains, degree of crosslinking and so forth, which in turn, are a reflection of the kinetic history of the reactions occurring during their formation.

The majority of reported studies on the mechanism of copolymerization have been based upon polymerization to low conversion. Relatively little effort has been devoted to the study of polymerizations to high conversion [112], and little attention has been directed to the question of whether mechanisms, which have been tested at low conversion are able to predict and/or describe copolymerization behavior at intermediate and high conversions [2,112].

To fully describe the free-radical copolymerization of vinyl monomers it is necessary to model conversion-dependent composition and conversion-dependent sequence distribution of copolymer chain and simultaneously, model time-dependence of the conversion. From these efforts it may be possible to solve the problems associated with the industrial production of certain types of copolymers and their final products.

Gao and Penlidis [112] reviewed high conversion free-radical copolymerization in bulk and in solution for a number of copolymer systems. They used the pseudo-kinetic rate constant method, proposed by Hamielec et al. [113], to describe the conversion of monomers. The onset of the gel effect and limiting conversion were predicted using the free volume approach of Marten and Hamielec [114]. Molecular weight averages, both, number and weight, were calculated from the population balances for radical and dead polymer molecules, by substituting pseudo-rate constants for rate constants in a homopolymerization scheme. Instantaneous and cumulative copolymer chain compositions as a function of monomer conversion have been approached from monomer reactivity ratios and rate of consumption of each monomer. Experimental data from different authors have been compared with predictions for 15 copolymer systems. Model predictions agree quite well with experimentally measured conversion, composition and molecular weight for acrylates and styrene copolymerization systems. However, copolymerization involving monomers such as acrylonitrile or 2-hydroxyethyl acrylate were found problematic. The Gao and Penlidis' treatment [112] has the merit to use database packages of homo- and copolymerizations to simulate experiments. The database could be utilized to predict the behavior of terpolymerization, since composition, sequence distribution and copolymerization rate in terpolymerization are entirely predictable, if it is assumed that there is no PUE using parameters measured from data for the constituent copolymerization [115,116]. In this way, very recently, Gaos and Penlidis [117] extend their model to terpolymerization of methyl methacrylate/butyl acrylate/vinyl acetate over the full conversion range. The model consistently delivered reliable predictions on conversion, composition and molecular weight averages in terpolymerizations performed in bulk and in solution.

However, the theoretical bases used by Gao and Penlidis [112] are not always appropriate and in many cases only a reasonable approximation of the real results can be obtained. In this way, it is now well documented that the overall propagation rate coefficient in copolymerization is dependent not only on monomer feed composition and monomer reactivity ratios, but also on the radical reactivity ratios. Furthermore, when the terminal model is applied, except for a few systems, estimated values of overall propagation rate coefficient in copolymerization are higher than the experimental ones. This fact has also been observed in terpolymerization experiments [118].

As widely recognized, the knowledge of the intermolecular (chemical composition and MWD) and the intramolecular (sequence distribution and tacticity) structure of copolymers is important because it provides information about the reaction mechanism occurring during polymerization. Besides it plays a key role in the understanding of relationship between the polymerization mechanism, molecular structure and properties [37]. The experimentally observed composition and structure variation with conversion will be compared with that predicted from reactivity ratios, statistical parameters and coisotacticity parameters estimated previously at low conversions. The effect of conversion on the cumulative copolymer composition as well as the stereochemical composition of copolymer chains has been approximated by a step function. Copolymerization theory allows deriving the amount of each monomer that is polymerized and the instantaneous copolymer composition and microstructure for each step, which can be accumulated over the conversion to yield integrated values.

The cumulative copolymer composition as a function of conversion for different mole fractions in the feed is approach using the MLTM and the monomer reactivity ratios. As an example Fig. 1 shows the experimental and predicted cumulative copolymer composition for 2-hydroxyethyl methacrylate (HEMA) with *t*-butyl acrylate (*t*BA) [119]. The solid lines were drawn according to the procedure given above, with reactivity ratios found at low conversion, i.e. $r_{\mathrm{HEMA}} = 1.792$ and $r_{t\mathrm{BA}} = 0.510$. It is clear that experimental and predicted data agree very closely.

Following this treatment the changes in cumulative copolymer composition have been reported for methyl methacrylate–methyl acrylate [120], 2-hydroxyethyl methacrylate–styrene [53], methyl methacrylate–butyl acrylate [121], di-*n*-butyl itaconate–methyl methacrylate [122] systems. O'Driscoll and Huang [123] have also described the changes in copolymer composition with increasing conversion for the copolymerization of styrene and methyl methacrylate. Experimental changes in copolymer composition with conversion in the acrylonitrile–styrene system have been measured by Hill et al. [2,124]. Since for the acrylonitrile–styrene system the explicit penultimate model describes the copolymer composition at low conversion, it has been used to predict the changes in copolymer composition following an interactive method similar to that previously described. The found values agree very closely to the predicted ones.

Considering that the formation probability of any sequence distribution is a function of the monomer feed mole fraction, during the copolymerization reactions at high conversion a change of instantaneous monomer feed is produced as the reaction processes and sequence distribution will vary from chain to chain depending when the chain is formed, i.e. at the beginning or near the end of the reaction [125]. The

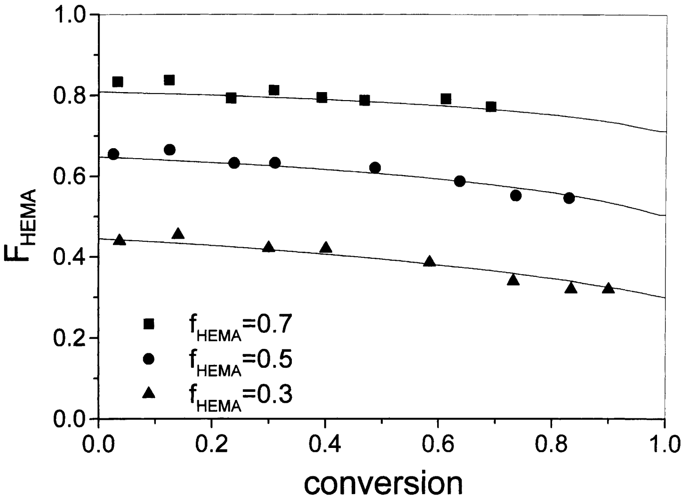

Fig. 1. Dependence of cumulative copolymer composition with conversion for the polymerization of the HEMA–*t*BA in DMF solution at 50 °C. Solid lines were calculated according to the MLTM with $r_{\mathrm{HEMA}} = 1.792$ and $r_{t\mathrm{BA}} = 0.510$. Reprinted from Polymer 2000;41:8155–8159. ©2000 with permission from Elsevier Science (Ref. [119]).

formation probability of the different centered triads has been calculated according to the monomer reactivity ratios, the conditional probabilities calculated from the reactivity ratios and the instantaneous monomer molar fractions in the feed. Introducing the corresponding equations can modify the step function previously described, which allow calculating the sequence distribution copolymer composition. To correlate the molar concentration of centered sequences with the statistical sequence distribution and stereochemical configuration of copolymer chains, an analysis has been carried out by making the following assumptions:

(a) With respect to the chemical composition or copolymer sequence, it is assumed that the copolymerization reaction is described by MLTM.

(b) From a statistical point of view, it is assumed that the configurational sequence distribution may be described according to Bernouillian statistics, with the isotacticity parameters σ_{11}, $\sigma_{12} = \sigma_{21} = \sigma$ as defined by Bovey [126] and Coleman [127] where σ_{ij} is the probability of generating a meso dyad between an growing radical chain end i and incoming monomer j.

From this set of stereochemical parameters, along with the average molar fractions in the monomer feed and the conditional probabilities calculated from the quoted reactivity ratios, the theoretical stereochemical composition can be obtained. As an example the peaks named I, II, III, IV and V, have been assigned to different configurational arrangement of HEMA (H)–*t*BA (A) copolymers [128]: peak I, centered at 0.85 ppm, is assigned to HHH triads in *rr* configuration. Peak II, centered at 0.92 ppm, is assigned to AHH/HHA in *rr* and *mr*/*rm* configuration. The peak III, centered at 0.99 ppm, is assigned to HHH with *mr*/*rm* configuration and to AHA with coheterotactic and cosindiotactic configuration. The peak IV, centered at 1.07 ppm is assigned to AHA in *mm* configuration along with AHH/HHA in *rm*/*mr* configuration. Finally peak V, from 1.10 to 1.22 ppm is assigned to HHH and AHH/HHA with *mm* configuration. Fig. 2 shows the experimental relative intensities (tactic triads molar fraction) of the different arrangements along with theoretical values as a function of the conversion for comonomer feed

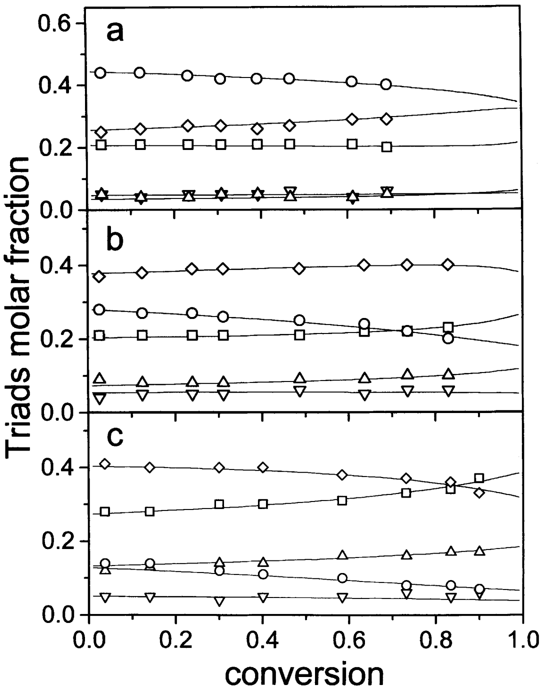

Fig. 2. Comparison between the observed and calculated HEMA-centered triad molar fractions obtained with increasing conversion, for the high conversion copolymerizations of HEMA and *t*BA carried out in DMF at 50 °C. (a) $f_{\mathrm{HEMA}} = 0.7$, (b) $f_{\mathrm{HEMA}} = 0.5$, (c) $f_{\mathrm{HEMA}} = 0.3$. Experimental triad molar fraction (○) I, (◇) II; (□) III; (△) IV and (▽) V. The predicted values (full lines) were calculated using the MLTM with $r_{\mathrm{HEMA}} = 1.792$ and $r_{t\mathrm{BA}} = 0.510$ along with the $\sigma_{\mathrm{HH}} = 0.17$ and $\sigma_{\mathrm{HA}} = \sigma_{\mathrm{AH}} = \sigma = 0.55$ obtained for copolymers produced at low conversions. Reprinted from Polymer 2000;41:8155–8159. ©2000 with permission from Elsevier Science (Ref. [119]).

composition $f_{\mathrm{HEMA}} = 0.7$, 0.5 and 0.3. The experimental and predicted values agree very closely which indicate that inter- and intramolecular structure of copolymers can be described by the MLTM over the entire range of conversion [119].

Comonomer sequence distribution over the full conversion range has been also reported for methyl methacrylate–methyl acrylate [120], and 2-hydroxyethyl methacrylate–styrene [53] systems.

Several models describe the glass transition temperatures of copolymer (T_g) taking into consideration the sequence distribution of the monomer units. Among all these models, the ones derived by Johnston [129], Barton [130] and Couchman [131], which correlate T_g to the dyad distribution in the instantaneous copolymer molecules, have good agreement with experimental T_gs [132,133].

Johnston [129] assumes that AA, AB or BA and BB dyads have their own glass transition temperature, with the overall T_g of a copolymer described by the following expression

$$\frac{1}{T_g} = \frac{w_A P_{AA}}{T_{gAA}} + \frac{w_B P_{BB}}{T_{gBB}} + \frac{w_A P_{AB} + w_B P_{BA}}{T_{gAB}} \tag{26}$$

where w_A and w_B are the weight fraction of two monomer units A and B. T_{gAA}, T_{gBB} and T_{gAB} denote the T_g contribution of AA, BB, and AB or BA dyads in the copolymer, and can be substituted by the T_g of A homopolymer, B homopolymer and the supposed T_g for the alternating AB copolymer, respectively. P_{AA},

P_{BB} and P_{AB} or P_{BA} are the probabilities of AA, BB and AB or BA dyads in the copolymer chain, respectively, and can be calculated by using the monomer feed compositions and monomer reactivity ratios [134]. T_{gAB} for AB copolymers is unknown, but they could be estimated from the experimental data of involved homopolymers and those of A–B copolymers using a linearized form of Johnston's equation [129].

It is important to know whether or not the results obtained at low conversion can be employed to predict the variation of T_g with conversion. To do this, it is necessary to assume that any macromolecule in the copolymer sample has its own glass transition temperature [135]. The objective of the simulation is to compute the overall mixture behavior of copolymer macromolecules produced through the process. The variation of T_g with conversion has been approximated using the step function previously described.

Experimental T_g data for methyl methacrylate (A)–butyl acrylate (B) copolymers, gathered with the theoretically estimated curves, are depicted in Fig. 3, where a reasonable agreement can be observed [136]. This means that Johnton's equation for the glass transition temperature of copolymer is able to explain the dependence between the glass transition temperature and both copolymer structure and conversion. In others words, the apparent glass transition temperature calculated, namely T_{gAB}, adequately fits the T_g variation of the copolymers at different conversions in a wide range of monomer feed compositions. Variation of glass transition temperature of copolymers with increasing conversion has been described for various copolymerization systems in others papers [122,133,137].

This approach could be useful to understand and predict the glass transition temperature of random copolymers over an entire conversion range. This could lead to an ability to select the appropriate conditions in the copolymerization process to synthesize a copolymer with desired structure and properties.

A model, which reproduces the variation of conversion against time is difficult, because of the uncertainty of the rate parameters values which usually, are both composition and conversion dependent. However assuming a first order monomer concentration, the copolymerization of two monomers A and B, either in presence or absence of solvent, may be, in a general sense, formally expressed in a way

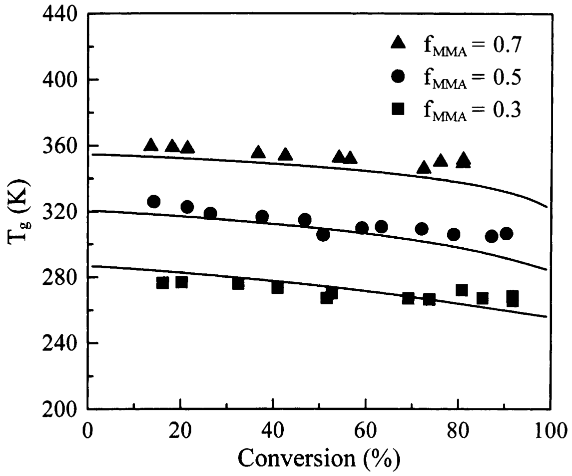

Fig. 3. Glass transition temperature for MMA–BA copolymers obtained in $[M] = 3\ \text{mol}\ l^{-1}$ benzene solution with different feed composition over the whole conversion range. Reprinted from J Polym Sci, Polym Phys 1999;37:2512–2520. ©1999 with permission of Wiley (Ref. [136]).

similar to that of the homopolymerization [80,123]

$$\ln\frac{1}{(1-x)} = 2\overline{k_\mathrm{p}}\frac{(2f(I_0))^{1/2}}{(\overline{k_\mathrm{t}}k_\mathrm{d})^{1/2}}\left[1-\exp\left(\frac{-k_\mathrm{d}t}{2}\right)\right] \tag{27}$$

where x is the overall conversion defined as the weight fraction of monomers converted to copolymer. $[I_0]$ is the initial concentration of initiator with a decomposition rate coefficient k_d, and efficiency factor, f. The average values of propagation and termination rate constants are expressed as $\overline{k_p}$ and $\overline{k_\mathrm{t}}$, respectively. Besides $\overline{k_\mathrm{p}}$ and $\overline{k_\mathrm{t}}$ are functions of conversion, because of composition drift.

From the polynomials of the semilogaritmic plot of conversion versus time and using Eq. (27) is possible to determine $\overline{k_\mathrm{p}}/\overline{k_\mathrm{t}^{1/2}}$ ratio as a function of monomer conversion. Considering the homopolymerization kinetic parameters for monomers A and B along with the monomer and radical reactivity ratios for the copolymer system, the variation of $w=\overline{k_\mathrm{p}}/\overline{k_\mathrm{t}^{1/2}}$ with conversion can be theoretically calculated from Eq. (19) considering the instantaneous monomer feed composition throughout the course of the polymerization. Although initiator efficiency f is known to be conversion dependent [138] for the calculation it is assumed, in agreement with O'Driscoll et al. [139], that k_d and f do not change appreciably over the course of copolymerization.

Comparison between the values deduced from experimental curves of methyl methacrylate–butyl acrylate copolymerization system [121] and those calculated following the penultimate effect model are given in Fig. 4, where values of $w=\overline{k_\mathrm{p}}/\overline{k_\mathrm{t}^{1/2}}$ versus percent of conversion were drawn. The dotted lines are the experimental data, and the solid lines are the simulation predictions. Independent of the monomer feed compositions, the simulation seems to predict $w=\overline{k_\mathrm{p}}/\overline{k_\mathrm{t}^{1/2}}$ reasonably well up to intermediate conversion. Beyond intermediate conversion simulation predicted values increase more markedly than the corresponding experimental quantity. A similar prediction has also been carried out for di-*n*-butyl itaconate–methyl methacrylate system [122]. In this case $w=\overline{k_\mathrm{p}}/\overline{k_\mathrm{t}^{1/2}}$ decrease with increasing conversion, but after intermediate conversion, the decrease for experimental values is more marked than for the corresponding theoretical one.

In order to explain the differences found between experimental and predicted values we must consider that theoretical calculations have been done by assuming values of homopolymer values of $k_\mathrm{p}/k_\mathrm{t}^{1/2}$ ndependent of monomer conversion. However, it has been shown that the termination rate constant is a function not only of the chain length and linear expansion coefficient of the polymer radical but also of the hydrodynamic radius of the chain segments, the chain flexibility and the solvent viscosity [140].

For high conversion bulk free-radical copolymerization of *p*-methylstyrene and acrylonitrile a kinetic model incorporating free-volume theory seems to account reasonably well for diffusion-controlled termination and propagation [141]. The model also accounts for segmental-diffusion control of termination at low conversion and termination by reaction diffusion at high conversions. The Marten–Hamielec model [114] based on the free-volume theory has been used to model high conversion copolymerization of the *n*-vinylpirrolidone–methyl methacrylate system [142] or predict the evolution of molecular weight and composition of styrene–methyl methacrylate copolymers [143] prepared at high conversions.

Studies at moderate or high conversion have been carried out to evaluate monomer reactivity ratios [144, 145]. In other cases the compositions of copolymer or terpolymer have been measured over the whole range of conversion [146]. The effect of the reaction medium on copolymerization has also been studied for the methacrylic acid–methyl methacrylate system [147] or for the copolymerization of acrylamide with various

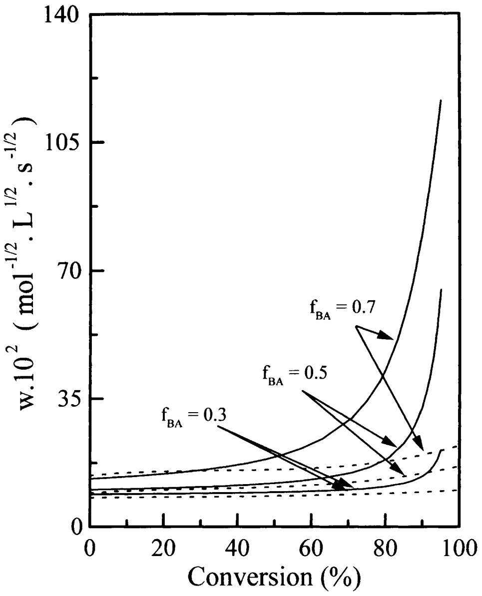

Fig. 4. Variation of the overall copolymerization parameter *w* with conversion in the copolymerization of MMA–BA at 50 °C in benzene solution: (—) theoretical data; (- - -) experimental data. Reprinted from J Polym Sci, Polym Chem 1997;35:1961–1965. ©1997 with permission of Wiley (Ref. [121]).

water-soluble monomers [148]. The kinetics of free-radical copolymerization of methyl methacrylate with various acrylates in the presence of a chain transfer agent (CTA) were investigated over the entire course of the reaction [149]. A displacement to higher conversion of the onset of the gel effect is observed in the presence of the CTA. The final conversion for a constant concentration of the CTA is independent of the initiator concentration, but is a function of polymerization temperature.

More studies of copolymerization at high conversion are required to get at least qualitative information on the general behavior. It must be recognized that these kinds of experiments are difficult to carry out. They are, however, important in the preparation of industrial products. So far, only the propagation step is relatively well known, but the knowledge of initiation and termination step is rather poor.

2.5. Transfer reactions in free-radical copolymerization

In any free-radical copolymerization, chain transfer reactions are important to control both molecular weight and MWD, since these parameters can influence many of the resulting polymer properties strongly (i.e. melt processability, solution viscosity, glass-transition temperature and gel content). As a result, molecular weight control is an important area in the field of addition polymerization, especially for many industrial applications where polymers with relatively low molecular weights are required.

A decrease in molecular weight is generally obtained via one of three routes:

1. By the addition of large amounts of initiator that increase the bimolecular termination reaction, and thus decrease the kinetic chain length.
2. By the addition of a CTA that causes the stopping of a growing polymer radical and the initiation of a new chain [150].

3. By using catalytic chain transfer agent (CCTA) which produce a dead polymer chain with a vinyl end-functionality and a monomeric radical [151].

There are two methods to determine chain transfer rate coefficients from the MWD. Traditionally, the magnitude of the chain transfer constant $C_T = k_{tr}/k_p$, where k_{tr} and k_p are the kinetic coefficient for transfer and chain propagation reactions, respectively, has been determined using the Mayo method [152]. This method has some disadvantages connected with the use of the number-average molecular weight ($\overline{M_n}$), since its values is very strongly affected by baseline fluctuations, and by manual setting of the integration limits in size exclusion chromatography [153,154]. Clay and Gilbert [155] proposed a new method to determine chain transfer constant based in the chain length distribution (CLD) which utilize the number MWD and has been recognized as the best way to obtain transfer constant to monomer and to chain tansfer agents [156].

Usually, in a free-radical copolymerization the rate parameters values are composition and conversion dependent. However, assuming a first order monomer concentration, the copolymerization transfer constant may be, in a general sense, formally expressed in a very similar way to that of polymerization. Thus the Mayo equation [152] may be expressed as

$$\frac{1}{\overline{\mathrm{DP}_n}} = \frac{1+\bar{\lambda}}{2}\,\frac{2\overline{k_t}R_p}{\overline{k_p^2}[M]^2} + \overline{C_S}\frac{[S]}{[M]} + \overline{C_T}\frac{[\mathrm{CTA}]}{[M]} + \overline{C_M} + \overline{C_I}\,\frac{\overline{k_t}R_p^2}{\overline{k_p^2}2\overline{fk_d}} \tag{28}$$

where $\overline{DP_n}$ is the number-average degree of copolymerization, R_p the copolymerization rate and $\overline{k_t}$ and $\bar{\lambda}$ are ($\overline{k_{t,d}} + \overline{k_{t,c}}$) and $\overline{k_{t,d}}/\overline{k_{t,c}}$, in which, $\overline{k_{t,d}}$ and $\overline{k_{t,c}}$ are the average values termination rate coefficients for disproportionation and combination, respectively, and $\overline{k_p}$, $\bar{f}$ and $\overline{k_d}$ are the average values of propagation coefficient, the initiator efficiency and the rate coefficient for initiator decomposition, respectively. $[S]$, $[M] = [M_i] + [M_j]$ and [CTA] are the concentration of the solvent, monomers and the CTA, respectively. $\overline{C_S}$, $\overline{C_T}$, $\overline{C_M}$ and $\overline{C_I}$ are the average transfer constants for solvent, CTA, monomers and initiator, respectively.

When the chain transfer constants for initiator, monomers and solvent are small compared with those of a CTA or a CCTA [157] Eq. (28) is reduced to

$$\frac{1}{\overline{\mathrm{DP}_n}} = \frac{1}{\overline{\mathrm{DP}_{n,0}}} + \overline{C_T}\frac{[\mathrm{TA}]}{[M]} \tag{29}$$

where $\overline{\mathrm{DP}_{n,0}}$ is the degree of polymerization of copolymer prepared in the absence of the CTA or CCTA ([TA] = 0).

In the presence of a TA, two reactions are important, i.e. the transfer reactions of the two different propagation radicals:

$$\sim\!\sim\!\sim A^{\bullet} + R-X \xrightarrow{k_{trA}} \sim\!\sim\!\sim A-X + R^{\bullet}$$

$$\sim\!\sim\!\sim B^{\bullet} + R-X \xrightarrow{k_{trB}} \sim\!\sim\!\sim B-X + R^{\bullet}$$

where R-X is TA and k_{trA} and k_{trB} are the transfer rate coefficient of the two homopolymers.

The average chain transfer rate coefficient, $\overline{k_{trT}}$, is related to the rate of chain transfer for the two above chain transfer reactions by the following expression

$$\overline{k_{\mathrm{trT}}} = k_{\mathrm{trA}}\frac{[\sim \mathrm{A}^{\cdot}]}{[\sim \mathrm{A}^{\cdot}]+[\sim \mathrm{B}^{\cdot}]} + k_{\mathrm{trB}}\frac{[\sim \mathrm{B}^{\cdot}]}{[\sim \mathrm{A}^{\cdot}]+[\sim \mathrm{B}^{\cdot}]} \tag{30}$$

as well as

$$\overline{k_{\mathrm{trT}}} = \phi_{\mathrm{A}}k_{\mathrm{trA}} + \phi_{\mathrm{B}}k_{\mathrm{trB}} \tag{31}$$

where ϕ_{A} is the fraction of growing chains that have an A radical end group, and $\phi_{\mathrm{B}} = (1 - \phi_{\mathrm{A}})$ is the fraction of B radical end groups [153,157].

The fraction of radical end groups can be calculated by considering the steady-state assumption in the radical concentrations, that is, the formation of A radicals through cross-propagation of B radicals is equal to the formation of B radicals trough cross-propagation of A radicals [150]

$$k_{p\mathrm{AB}}[\sim \mathrm{A}^{\cdot}][\mathrm{B}] = k_{p\mathrm{BA}}[\sim \mathrm{B}^{\cdot}][\mathrm{A}] \tag{32}$$

which can be rearranged to obtain

$$A_{\mathrm{A-B}} = \frac{[\sim \mathrm{A}^{\cdot}]}{[\sim \mathrm{B}^{\cdot}]} = \frac{\overline{k_{p\mathrm{AA}}}\bar{r}_{\mathrm{B}}f_{\mathrm{A}}}{\overline{k_{p\mathrm{BB}}}\bar{r}_{\mathrm{A}}f_{\mathrm{B}}} \tag{33}$$

The values of $A_{\mathrm{A-B}}$ depends on the average homopropagation rate coefficients $\overline{k_{p\mathrm{AA}}}$ and $\overline{k_{p\mathrm{BB}}}$, and hence on the values of the radical reactivity ratios, s_{A} and s_{B}. From this expression, the fraction of A radical end groups can be calculated [153]

$$\phi_A = \frac{A_{\mathrm{A-B}}}{1 + A_{\mathrm{A-B}}} \tag{34}$$

It should be noted here, that even if PUEs in chain transfer reactions are neglected, PUEs are still operative in the propagation step, and hence the average chain transfer constant for the two propagating radicals contains the average homopropagation rate coefficient.

In such a copolymerization the average chain transfer rate coefficient ($\overline{k_{\mathrm{trT}}}$) is a function of the molar fractions of the monomers and the individual chain transfer rate coefficients k_{trA} and k_{trB}. Furthermore, the average propagation rate coefficient ($\overline{k_{\mathrm{p}}}$) is also a function of monomers and radical reactivity ratios, monomer feed composition and individual propagation rate constant coefficients. Therefore $\overline{k_{\mathrm{trT}}}/\overline{k_{\mathrm{p}}}$ can only be obtained from the MWD[1] if the pertaining copolymer samples were obtained at low conversions, since the generally occurring composition drift will change the values of $\overline{k_{\mathrm{trT}}}$ and $\overline{k_{\mathrm{p}}}$ but very probably not to equal extents. So that the average chain transfer constant becomes dependent on conversion. It should be emphasized that the determination of $\overline{C_{\mathrm{TA}}} = \overline{k_{\mathrm{trT}}}/\overline{k_{\mathrm{p}}}$ gives average values.

When the copolymerization is carried out in the absence of transfer agent the determination of chain transfer to monomers is an important parameter to model the rate-determining kinetic mechanisms. Assuming a terminal model for transfer reaction, in a copolymerization reaction each radical chain end

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[1] An important factor in the accuracy of $\overline{k_{\mathrm{tr}}}/\overline{k_{\mathrm{p}}}$ obtained from these experiments is largely governed by the calibration of the SEC system. This can become a major problem especially for copolymer samples in which calibration curve is usualy expressed as a simply weighted average of the respective homopolymers calibration curve. More accurate results can be obtained using a SEC instrument with on-line low-angle light scattering and differential viscometer in addition to the standard differential difraction index detector.

suffers transfer reactions towards two entities, i.e. the two different monomers. Consequently, copolymerization chain transfer reactions are [158]

$$\sim\!\sim A^{\bullet} + A \xrightarrow{k_{\mathrm{trAA}}} \textit{polymer} + A_1^{\bullet}$$

$$\sim\!\sim A^{\bullet} + B \xrightarrow{k_{\mathrm{trAB}}} \textit{polymer} + B_1^{\bullet}$$

$$\sim\!\sim B^{\bullet} + A \xrightarrow{k_{\mathrm{trBA}}} \textit{polymer} + A_1^{\bullet}$$

$$\sim\!\sim B^{\bullet} + B \xrightarrow{k_{\mathrm{trBB}}} \textit{polymer} + B_1^{\bullet}$$

The average chain transfer rate coefficient to monomers i and j can be expressed as

$$\overline{k_{\mathrm{tr}}} = \overline{k_{\mathrm{tr}i}}f_i + \overline{k_{\mathrm{tr}j}}f_j = (k_{\mathrm{tr}ii}\phi_i + k_{\mathrm{tr}ji}(1-\phi_i))f_i + (k_{\mathrm{tr}ij}\phi_i + k_{\mathrm{tr}jj}(1-\phi_i))f_j \tag{35}$$

where $\overline{k_{\mathrm{tr}i}}$ is the average chain transfer rate coefficient to monomer i, f_i is the molar fraction of monomer i and $k_{\mathrm{tr}ii}$ and $k_{\mathrm{tr}ij}$ are the homo and cross-chain transfer rate coefficients from a polymeric with terminal unit i to monomer j, respectively.

Only in a few cases the determination of chain transfer coefficients has been applied to transfer in copolymerization. Rudin et al. have described the determination of chain transfer coefficients to monomers in styrene–α-methylstyrene [159], styrene–methyl methacrylate [160] and styrene–butyl acrylate [161] systems.

Chain transfer to monomer in low conversion emulsion copolymerization of styrene (S) with methyl acrylate (MA) and of S with methyl methacrylate (MMA) of various compositions, prepared with variable initiator concentration, has been recently analyzed [158]. For both systems, the chain transfer coefficient linearly increases with the MA or MMA molar fraction in the feed.

Assuming the above describes a model for the S–MA system, the observed increase in the average chain transfer coefficient when the MA molar fraction in the feed increases is due to a combined effect of the chain transfer coefficient for MA (k_{trMAMA}) and the fraction of MA radical end groups. k_{trMAMA} is higher than k_{trSS}. On the other hand, only ϕ_{MA} has significant values for higher MA molar fraction in the feed. Consequently, except for high MA molar fraction in the feed, the average copolymerization chain transfer coefficient is governed by the k_{trSS} and the k_{trSMA}. A rather similar behavior is observed for S–MMA system, but a more shallow increase of average copolymerization chain transfer coefficient with MMA molar fraction in the feed is observed as a consequence of the lower difference in homopolymerization chain transfer coefficient and a slightly higher value of ϕ_{MMA} compared with ϕ_{MA}. From the data obtained and considering the terminal model the $k_{\mathrm{tr}ij}$ can be calculated. The value of k_{trSMA} has been estimated to be 20 times lower than k_{trMAMA}, whereas k_{trSMMA} has a value similar to k_{trMMAMMA}.

The study of chain transfer to an added CTA, under the so-called ‘moderated copolymerization’ experimental conditions, was first reported by Bamford et al. [162–164]. They based their work on the terminal model for the propagation reactions, and derived equations to describe chain transfer to a very reactive substrate (CTA). From these equations, C_A and C_B, the chain transfer constants of both $\sim A^{\cdot}$ and $\sim B^{\cdot}$ type terminal radicals to CTA [162], were determined. This method has been applied to the system S–MA with carbon tetrabromide (CBr_4) as CTA [162]. When the method was applied to the system S–MMA with CBr_4, it was observed that the chain transfer constant depended on the molar ratio S–MMA, and a PUE was invoked to explain this behavior [163]. However, this effect was neither observed in the S–MMA system with butane thiol nor in the S–MA system with either CBr_4 or butane thiol [164].

The average chain transfer constant as a function of the monomer feed composition has been determined in the copolymerization of S with MMA for a CCTA, bis-[(difluoroboryl)diphenylglyoxymato] cobalt(II) (COPhBF) [153]. Contrary to other systems in which a dependence between chain length and copolymer composition has been observed [62,63], for S–MMA system copolymer composition is independent of the chain length. The average chain transfer constant decreases as the fraction of styrene in the monomer feed increases. This trend can be explained considering not only the monomer chain transfer coefficients and the molar fraction of propagating radicals, but also the overall copolymerization propagation coefficient. Although the values of ϕ_S are always larger than the fraction of S in the monomer feed the k_{trMMA} for the transfer reaction between MMA with COPhBF is 50 times higher than k_{trS} for the transfer reaction between S and COPhBF. Then, the overall chain transfer coefficient will be governed by more than 95% by the MMA ending radical, and increases as a function of the MMA molar fraction in the feed. Since the overall propagation for the S–MMA system decreases as the S molar fraction in the feed increases $\overline{C_T}$ decreases in the same way.

The copolymerization in benzene solution of S–MMA has been studied in the presence of *n*-dodecanethiol (DDT) [165]. Under these experimental conditions, the copolymer composition and stereochemical configuration are also independent of the copolymer chain length but contrary to that observed when a COPhBF is used, the $\overline{C_T}$ values increase with the S molar fraction in feed. This fact is a consequence of the fact that the chain transfer rate coefficient of DDT towards MMA is eight times lower than that for S [166].

When the copolymerization of S–MMA is carried out in the presence of carbon tetrachloride or carbon tetrabromide the values of chain transfer constant increase as S molar fraction in the feed does [167]. However, $\overline{C_T}$ experimental values are far from those predicted with both, the terminal model and a model in which no PUE is considered for transfer, but a PUE is included in the propagation. Harrison et al. [167] proposed a new chain transfer model with PUE in both the chain transfer and the propagation reactions. In the model, four new chain transfer constants are defined and is observed that chain transfer reaction of S–S-terminated radicals are faster than that of MMA–S-terminated radicals. The nature of the CTA and the increase in the magnitude of both, the chain transfer and the PUE when the copolymerization is performed in *N*,*N*′-dimethylformamide (a polar solvent) compared to the bulk experiments suggest the involvement of a polar transition state in the transfer and a polar contribution to the PUE.

Although the overall copolymerization chain transfer constant when CTA or CCTA are used is dependent on the overall radical concentration and the homopolymer chain transfer coefficients, the mechanisms of the conventional and catalytic chain transfer differ. Consequently, it is important to know how this variation affects the final molecular structure and the resulting polymer properties. Heuts et al. [168] compare the influence of a conventional CTA, DDT, with that of a CCTA, COPhBF, in the terpolymerization of styrene–methyl methacrylate–2-hydroxyethyl methacrylate (S–MMA–HEMA). The copolymerization rate is hardly affected by the nature of the transfer agent. However, when DDT is used as transfer agent $\overline{\mathrm{DP}_\mathrm{n}}$ increases and MWD broadens as conversion increases, but both parameters remain unchanged when COPhBF is used. These facts are explained considering that due to the differences between the rate of consumption for DDT and for S–MMA–HEMA monomers the [DDT]/[monomers] ratio decreases and therefore $\overline{\mathrm{DP}_\mathrm{n}}$ increases. The invariant $\overline{\mathrm{DP}_\mathrm{n}}$ and MWD when COPhBF is used as CCTA is not clear, since as CCTA is not consumed the [COPhBF]/[monomers] ratio should increase and consequently $\overline{\mathrm{DP}_\mathrm{n}}$ should decrease. The differences in the nature of the end-groups, saturated chain ends using DDT or unsaturated chain ends using COPhBF, are manifested in the thermal stability. Terpolymers synthesized using COPhBF are slightly less stable than the products formed in the presence of DDT.

Kukulj et al. [169] studied $\overline{C_\mathrm{T}}$ in the copolymerization of S with α-methylstyrene (αMS) in the presence of bis(boron difluorodimethylglyoxymate)cobaltate(II) (COBF). As in the MMA–S system, $\overline{C_\mathrm{T}}$ varies with monomer feed composition. Its value increases when the αMS molar fraction in the feed increases. The values found were in good agreement with model predictions since $k_{\mathrm{tr}\alpha\mathrm{MS}}$ has a value of $\sim 10^6\ \mathrm{l\ mol^{-1}\ s^{-1}}$ whereas k_{trS} has a value of $\sim 10^3\ \mathrm{l\ mol^{-1}\ s^{-1}}$. Furthermore, αMS is the dominant radical chain end even at fractions of αMS in the monomer feed as low as 0.1. Then, a significant increase of $\overline{C_\mathrm{T}}$ can be expected with small addition of αMS to S. However, the observed increase in $\overline{C_\mathrm{T}}$ is higher than that expected considering the monomer chain transfer coefficient and the molar fraction of chain end radicals. This behavior is due to a combined effect, the increase in $\overline{k_{\mathrm{trT}}}$ and the continuous reduction of $\overline{k_\mathrm{p}}$ as the αMS molar fraction in the feed increases [103].

In a recent publication [170], the average chain transfer constant in the copolymerization of methyl methacrylate (MMA) and butyl acrylate (BA) to dodecanethiol (DDT) was determined. It was found that although the chain transfer coefficient for DDT to BA is 90 times higher than that corresponding to MMA, $\overline{C_\mathrm{T}}$ only slight changes with the monomer feed composition. However, this fact may be only apparent since the average chain-transfer constant is a relationship between two reaction rate coefficients that is transfer and propagation coefficients. Considering that the average copolymerization propagation coefficient ($\overline{k_\mathrm{p}}$) largely increases with the increase of BA molar fraction in the feed, the average chain transfer rate coefficient ($\overline{k_\mathrm{tr}}$) will increase in the same way. Its values compare well with those theoretically calculate.

Considering that ϕ_S is dependent on the values of radical reactivity ratios s_i, Heuts et al. [91,153] suggest that measurements of the average transfer coefficient as a function of monomer feed composition can be used as a new way to calculate radical reactivity ratios. To do this it is assumed that transfer reactions follow the terminal model whereas propagation reactions are governed by the penultimate model. From Eq. (31) the molar fraction of radical chain end, ϕ_i, can be evaluated as a function of monomer feed composition knowing the $\overline{C_\mathrm{T}}$ and $k_{\mathrm{tr}i}$ values. At the same time ϕ_i can be theoretically determined from Eq. (34) knowing the homopropagation rate constant, the monomer reactivity ratios and using different set of radical reactivity ratios, which fit the experimental molar fraction of radical chain end as a function of monomer feed.

Besides the molecular weight control, CCTAs allow the preparation of copolymers with a vinyl end-functionality. The nature of this end-functionality can be predicted and controlled by using the knowledge of conventional free-radical copolymerization [153,169,171]. The particular nature of the vinyl endgroup is important in order to use the copolymers for a post-polymerization modification. Thus monomers with α-methyl group produce an external vinyl group, which may be important for the modification of oligomeric copolymers prepared in the presence of a CCTA. Heuts et al. [171] indicate that the production of a particular end group is dependent not only on a high chain transfer constant for a specific radical but also on a high enough relative concentration of this particular radical. When the relative concentration of $\sim A^{\cdot}$ propagating radical is always larger than the fraction of A in the monomer feed and at the same time the average chain transfer constant increases with the molar fraction of A in the feed, nearly all the unsaturated endgroups will originate from the catalytic chain transfer process on monomer A. Furthermore Chiefari et al. [172] observed that the macromonomer purity is also influenced by the cobalt complex concentration, the type of cobalt complex and the reaction temperature.

Chain transfer reactions in copolymerization are important not only to control molecular weight, but also in some cases as a relatively simple and clean method to prepared low-molecular weight end-functionalized polymers.

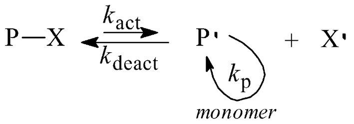
3. Living/controlled statistical free-radical copolymerization

3.1. General aspects

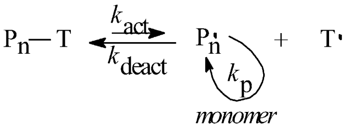
For many years a general method to obtain statistical copolymers with low polydisperity, accurate control of molecular weight and chain end has been a goal for synthetic polymer chemists. Until a few years ago copolymers with such characteristics could only be obtained using anionic [173], cationic [174] and group transfer [175] procedures. However, these methods are not well suited for preparation of well-defined statistical copolymers from vinyl monomers, such as styrenics and acrylates. In the 1990s, several methods were developed that enable controlled radical copolymerization. These methods include stable free-radical polymerization (SFRP), atom transfer radical polymerization (ATRP) and reversible addition–fragmentation chain transfer (RAFT). Using these polymerization methods, the molecular weight of the polymers linearly increases with conversion and the polydispersities are well below 1.5.

The three principal mechanisms that have been put forward to achieve living free-radical polymerization are mechanistically based on the common concept of an alternating activation–deactivation process (see Scheme 1), in which a dormant species P-X is reversibly activated to form a polymer radical $P^{\cdot}$ by thermal, photochemical and/or chemical stimuli [176].

To be effective in controlling a radical polymerization there are two necessary conditions for the equilibrium as shown in Scheme 1. First, the equilibrium between dormant and active (free radical) species must lie strongly to the side of the dormant species to assure that the overall concentration of propagating radicals will remain very low and that the rate of irreversible termination will be negligible relative to the apparent rate of polymerization. Second, the rate of exchange between dormant and active species must be faster than the rate of propagation to assure that all polymer chains have equal probability of adding monomer. If these stipulations are accomplished, then a living radical polymerization yielding polymers with a wide range of molecular weights and narrow MWDs is possible [177].



Scheme 1. General scheme for living/controlled free-radical polymerization.



Scheme 2. Stable free-radical polymerization.

The first such mechanism, SFRP (see Scheme 2), is a polymerization with reversible termination by coupling with a persistent radical (e.g. nitroxide). Currently, the best example in this class is alkoxyamine-initiated or nitroxide-mediated polymerization first described by Rizzardo et al. [178], and later developed by Georges [179] and Hawker [180].

The key reactions in this system have been shown to be the alternating activation–deactivation process, in which the polymer-nitroxide adduct P-T (dormant species) is reversibly activated by thermal homolysis into the polymer radical ($P^{\cdot}$) and the stable nitroxyl ($T^{\cdot}$). This dramatically lowered the concentration of active chain species in the polymerization system and, coupled with the inability of the nitroxide radicals to initiate new chains lead to a controlled polymerization [176]. These activation–deactivation cycles allow all the chains to propagate at nearly equal rate, thus controlling the chain length and its distribution.

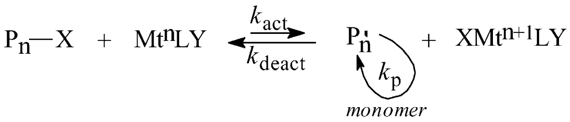
The second mechanism, ATRP (see Scheme 3), is a radical polymerization with reversible termination by ligand transfer from a transition metal complex [176,177] ATRP is based on the catalyzed reversible cleavage of the covalent bond in the dormant species through a one electron redox process.

This method utilizes a reversible halogen atom abstraction step, in which a lower oxidation state metal (Mt^n complexed by a ligand LY) reacts with an alkyl halide (P_n-X) to generate a radical ($P_n^{\cdot}$) and a higher oxidation state metal complex ($XMt^{n+1}LY$, k_{act}). This radical then adds monomer to generate the polymer chain (k_p). The higher oxidation state metal can then deactivate the growing radical to generate a dormant chain and the lower oxidation state metal complex (k_{deact}) [181,182].

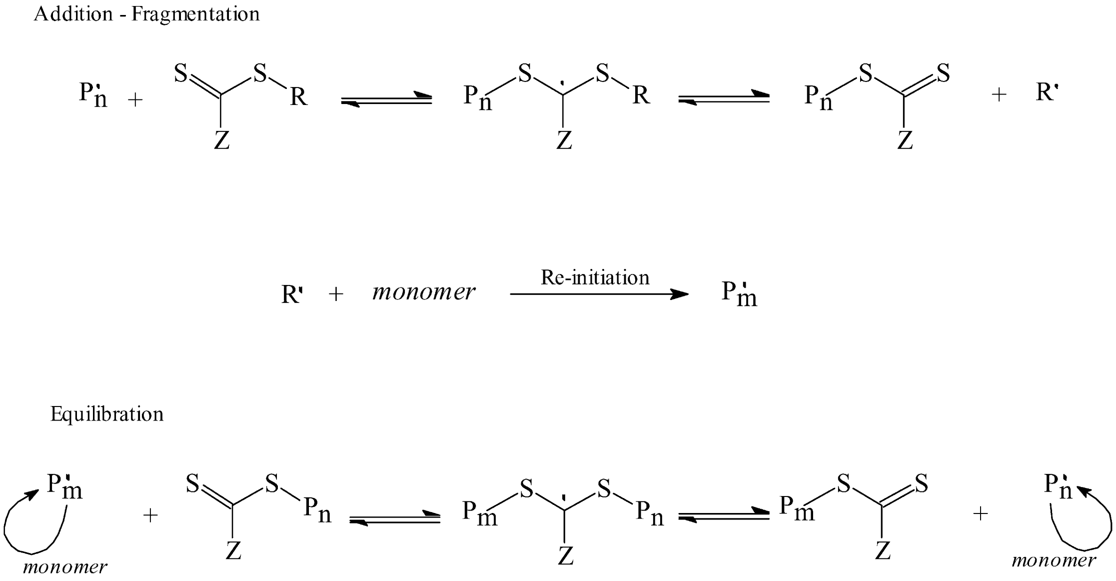
The third mechanism, RAFT (see Scheme 4), for achieving living character is free-radical polymerization with reversible chain transfer [183].

The initiation system consists of a standard free-radical initiator and a suitable thiocarbonylthio compound, which acts as highly efficient reversible addition–fragmentation CTA and provides the polymerization with living characteristics. The sequence of events as shown in Scheme 4, relies first on the chain transfer of active species ($P_n^{\cdot}$) to the thiocarbonylthio compound, which then undergoes fragmentation to reinitiate polymerization. The polymeric thiocarbonylthio compound [S=C(Z)S-P_n] is the dormant species. Once the thiocarbonylthio compound is consumed, equilibrium is established between active and dormant species [183].

Although it is generally accepted that living/controlled free-radical polymerization (LCRP) has a similar mechanism than that operating in conventional free-radical polymerization, because transfer and termination reaction practically disappear, in LCRP some subtle differences can be observed. Thus, in



Scheme 3. Atom transfer radical polymerization.



Scheme 4. Reversible addition–fragmentation chain transfer.

conventional radical copolymerization, the lifetime of a polymer radical is typically in the order of a second, in which the initiation, propagation and termination occurs, given a dead polymer with a degree of polymerization (DP) of about 10^3–10^4. Such dead polymers are produced at every instant and are accumulated in the system throughout the course of the copolymerization. The copolymer composition will vary from chain to chain and will depend on the moment in which they were formed. This means that if the copolymer composition is analyzed, the observed composition is necessarily an average of all the chain polymers produced at a specific conversion.

Assuming that in LCRP the growing radical has the same reactivity, e.g. the same rate coefficient for propagation and termination as in conventional, the growth of a chain to reach a DP value of 10^3 may take several hours. This fact indicates that a living chain spends most of the polymerization time in a dormant state. Furthermore, as the vast majority of chains do not irreversibly terminate, but grow gradually throughout the polymerization, the change in monomer feed is recorded in the polymer chain itself and not among the various chains. This means that copolymer chains contain a gradient of composition since the monomers are consumed at different rates. Then, if the copolymer composition were analyzed, the observed composition would be the same as that observed in conventional copolymerization, but is an average of the individual chain composition instead of an average of many individual copolymer chains [176,184].

Usually, in conventional free-radical copolymerization monomer reactivity ratios are measured by fitting the copolymer composition at low conversion as a function of initial monomer feed composition. However, in LCRP the copolymer chain is slowly formed throughout the reaction and measurements of the copolymer chain composition at low conversion can be affected by the structure of the initiator, which may preferentially react with one comonomer. Therefore to obtain reliable results it is necessary to measure the cumulative copolymer composition from 10–20% to high conversion [185,186]. Consequently, it is necessary to make use of the integrated form of the copolymer composition equation [187,188]. Although a number of papers indicate that for copolymers performed by LCRP copolymer chain composition data as a function of initial monomer feed composition can be described throughout the copolymerization by the MLTM, this has to be confirmed. Fukuda et al. [80] have pointed out that many of the kinetic aspects in free-radical copolymerization are governed by the relative fractions of propagating radicals with different terminal units. In conventional free-radical copolymerization the two cross-propagation reactions are the only reactions from which the relative radical concentration can be determined. Assumption of steady-state concentration involves that the formation of $A^{\cdot}$ radicals through cross-propagation of $B^{\cdot}$ radicals equals the formation of $B^{\cdot}$ radicals through cross-propagation of $A^{\cdot}$ radicals (see Eq. (32)) [150] and the ratio between two radicals can be expressed by Eq. (33).

However, in LCRP the two monomers which participate in the copolymerization may have equilibrium reactions between active and dormant species [189,190].

Thus following Scheme 2 in SFRP the two equilibriums may be expressed by

$$K_i = \frac{[\mathrm{P}^{\cdot}_{ni}][\mathrm{T}]}{[\mathrm{P}_{ni}\text{-}\mathrm{T}]} \tag{36}$$

whereas considering Scheme 3 for ATRP the two equilibriums may be expressed as

$$K_i = \frac{[\sim \mathrm{P}^{\cdot}_{ni}][\mathrm{Cu(II)X/2L}]}{[\sim \mathrm{P}_{ni}\text{-}\mathrm{X}][\mathrm{Cu(I)/2L}]} \tag{37}$$

where K_i is the equilibrium constant involving radicals with A or B terminal units and $\sim\mathrm{P}^{\cdot}_{ni}$ is the growing radical A or B.

In LCRP the disappearance rate of $\sim\mathrm{P}^{\cdot}_{ni}$ radicals should include the reverse reaction of Schemes 2 and 3, but the formation rate of $\sim\mathrm{P}^{\cdot}_{ni}$ radicals should also include the forward reaction of Schemes 2 and 3 [189]. As in equilibrium the rate of forward and reverse reactions are equal, the two terms cancel and consequently $A_{\mathrm{A-B}}$, the ratio of the concentration of the two different propagating radicals, are the same for both, conventional and LCRP copolymerization, which means that instantaneous composition in LCRP should be the same as in conventional free-radical copolymerization. However, from copolymerization experiments only an average equilibrium is accessible. This average equilibrium is weighted over the fractions of the two radical chain ends.

Chambard and Klumperman [185] have confirmed the above conclusion. These authors used simulations to evaluate the influence of activation and deactivation differences on the copolymerization kinetics and therefore on the reactivity ratios. They observed that in the copolymerization of styrene with butyl acrylate the radical ratio between the growing styrene ending radicals ($\sim\mathrm{S}^{\cdot}$) and the growing butyl acrylate ending radicals ($\sim\mathrm{BA}^{\cdot}$), ($\sim\mathrm{S}^{\cdot}/\sim\mathrm{BA}^{\cdot}$), is always the same no matter the difference between the activation of both dormant species is. In a similar way Ziegler and Matyjaszweski [186] have also simulate the ATRP copolymerization of methyl methacrylate (MMA) and butyl acrylate (BA) and observed that the relationship

$$\frac{k_{p\mathrm{MMABA}}[\sim \mathrm{MMA}^{\cdot}][\mathrm{BA}]}{k_{p\mathrm{BAMMA}}[\sim \mathrm{BA}^{\cdot}][\mathrm{MMA}]}$$

will equal unity when the cross-propagation is at equilibrium. Consequently the MLTM can be utilized to describe the copolymer composition.

Another important aspect of the copolymerization, well recognized nowadays, is the copolymerization rate, because of the necessity of accurate kinetic modeling, suitable to describe the whole course of the copolymerization reaction.

As it is well known in conventional copolymerization of two monomers the overall polymerization rate, R_p, is given by [80]

$$R_p = \overline{k_p}([A^{\cdot}] + [B^{\cdot}])([A] + [B]) \tag{38}$$

In LCRP copolymerization [189] the total radical concentration, which determine the copolymerization rate, is regulated by the equilibrium given by Eqs. (36) or (37). The pseudo-first order behavior of R_p [189] leads to a pseudo-first order rate coefficient, $\overline{k_p^{app}}$, which is expressed by

$$\overline{k_p^{app}} = \overline{k_p}([A^{\cdot}] + [B^{\cdot}]) \tag{39}$$

where $\overline{k_p}$ is the average propagation rate coefficient. In LCRP copolymerization the apparent rate coefficient is determined from the slope of a semilogaritmic plot of overall monomer conversion versus time, whereas in conventional copolymerization the average propagation rate coefficient can be obtained for example by pulsed laser copolymerization experiments.

Therefore in LCRP copolymerization the total radical concentrations can be obtained from

$$[A^{\cdot}] + [B^{\cdot}] = \frac{\overline{k_p^{app}}}{\overline{k_p}}$$

To the best of my knowledge most of the LCRP copolymerization experiments do not study the variation of copolymerization rate as a function of monomer feed composition, and only a few [186,191] have compared the behavior observed in LCRP with those observed in conventional copolymerization. However, due to the equilibrium of the different species, the total radical concentration may be dependent on the experimental conditions, even though the ratio between two radicals are the same for conventional and LCRP copolymerization. In this sense the simulations carried out by Chambard and Klumperman [185] have demonstrated that the ratio of dormant species is very dependent on the differences between activation/deactivation coefficients, therefore the overall radical concentrations should also be dependent. This fact is very important when the overall copolymerization rate is studied since differences in overall radical concentrations can lead to copolymerization rate values, which may differ from that observed in conventional copolymerization.

3.2. Some examples of statistical stable free-radical copolymerizations

Most nitroxyl radical-mediated polymerization systems use 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO) as the persistent radical. The initiating systems consist of either a combination of a conventional radical initiator with TEMPO (the optimum ratio is apparently 1.3:1) or a preformed alkoxyamine.

This kind of initiator systems have been proved to be effective in controlling not only styrene homopolymerization, but also copolymerization of styrene and their derivatives with other monomers such as acrylates, methacrylates or acrylonitrile when comonomer composition is relatively rich in styrene monomer [192]. However, the TEMPO derivative systems have achieved limited success in controlling the homopolymerization of other monomers [192].

Examples of copolymerization of styrene (S) with their derivatives such as 4-hydroxystyrene (4-HS)

[193], 4-acetoxystyrene (4-ACS) [193] or chloromethylstyrene (CMS) [194] have recently been reported. In all cases well-defined statistical copolymers were obtained.

Copolymerization of styrene with other monomers have some limitations. Then, bulk copolymerization of styrene (S) with methyl methacrylate (MMA) has been carried out at 125 °C using the hydroxy-functional 2-phenyl-2-(2′,2′,6′,6′-tetramethylpiperidinyloxy)-ethanol (**1**) as initiator [195]. For 0.8 and 0.7 styrene molar fractions in the feed the number average molecular weight linearly increases with monomer conversion, present low polydispersities and agree well with those theoretically expected. As the styrene molar fraction in feed decreases, the polydispersity increases and differences between experimental and theoretical values of M_n increase. A similar trend has been observed in the thermal copolymerization of S–MMA carried out at 130° presence of TEMPO [196]. Similar to the S–MMA system, the living/controlled copolymerization of S with butyl acrylate (BA) using the derivative **1** as unimolecular initiator shows that experimental and theoretical M_ns agree well for high S molar fractions in the monomer feed, whereas the agreement is lower when the BA molar fraction in the feed increases [197]. The thermal copolymerization of S–BA in the presence of TEMPO shows similar behavior as those described for the copolymerization mediated by **1** [196]. Recently, copolymerization of S with MMA and methyl acrylate (MA) has been carried out using 1-phenyl-1-(2′,2′,6′,6′-tetramethylpiperidinyloxy)-ethane (**2**) as initiator [198]. It is observed that for a long copolymerization time (16 h) the overall monomer conversion decreases as the MMA or MA molar fraction in the feed increases. This fact has been interpreted considering that the copolymerization rate is a function of the growing radical concentration. Then, if the radicals are formed not only by alkoxyamine homolysis but also by thermal self-initiation, a decrease of S molar fraction in the feed gives rise to a decrease of the thermal self-initiation and consequently, to a decrease of the copolymerization rate. The behavior of the molecular weight and the polydispersity index as a function of styrene monomer feed is similar to other styrene–meth(acrylate)–alcoxamine systems. The evolution of monomer conversion, molecular weight and polydispersity index as a function of copolymerization time is described for 0.5 S monomer feed for both copolymerization systems. A rapid increase of monomer conversion is obtained initially (60 and 40% within 4 h for S–MA and S–MMA systems, respectively) and thereafter a slower increase (75 and 49% after 16 h for S–MA and S–MMA systems, respectively) is found. Molecular weight linearly increases with polymerization time but is not in agreement with the theoretically calculated values. Polydispersity index is higher for the S–MMA system than for the S–MA system and, in addition a slight increase of polydispersity with time is observed for the S–MMA system.

Living/controlled free-radical copolymerization of S with butyl methacrylate (BMA) has been carried out by Schmidt-Naake et al. [199] using TEMPO capped polystyrene as macroinitiator (PST-TEMPO) and BPO/TEMPO as bimolecular initiator [191]. In the first case [199], only a fraction of 0.8 of S monomer in the feed is studied at relatively low monomer conversion (15–20%) using different amounts of macroinitiator. The copolymerization rate is independent of the macroinitiator concentration and its values are similar to those obtained in the thermal copolymerization. This behavior is explained considering that initiation is mainly due to the thermal self-initiation of styrene. M_n linearly increases up to 15–20% monomer conversion. On the other hand M_n as well as the polydispersity index decreases as the macroinitiator concentration increases [199]. The copolymerization of S–BMA system carried out in the presence of the bimolecular initiator is carried out at 130 °C after a pre-heating time of 1 h at 95 °C [191]. The copolymerization rate, contrary to conventional free-radical copolymerization, decreases as the BMA molar fraction in the feed increases, which is attributed to a lack of continuous thermal self-initiation. The decrease in copolymerization rate is correlated with a loss of reaction control, since the polydispersity index becomes larger as the BMA molar fraction in the feed increases. The monomer conversion as a function of polymerization time for an equimolar monomer feed is followed using the bimolecular initiator system along with different concentrations of dicumylperoxide (DCP). The use of DCP notably increases the copolymerization rate, while the number average molecular weight does not change with DCP concentration and linearly increases with polymerization time. The polydispersity index is similar to that obtained in the absence of DCP [191].

Block copolymers comprising styrene–acrylonitrile (S–AN) statistical copolymer have been synthesized by Fukuda et al. [200] using PS-TEMPO adducts. Copolymer microstructure is the same as that obtained by conventional copolymerization. Considering that the PS-TEMPO adduct gave no homopolymers with AN, Fukuda et al. [200] suggested that the PUE, which strongly affects the radical reactivity may have something to do with the dissociation of TEMPO adducts of the otherwise undissociative radicals.

Brinkmann-Regel and Niessner [201] have copolymerized S–AN using TEMPO as a stable free radical. For an azeotropic composition the number average molecular weight linearly increases with the copolymerization time up to a conversion of 60%, afterwards M_n levels off to smaller values. This behavior is attributed to side reactions that occur at long reaction times. Concurrently, the polydispersity index increases at high conversion, but remains lower than 1.5 for conversions up to approximately 70%. At longer reaction times a deviation from linearity of the kinetic plot is observed. A comparative study at low conversion between living and conventional free-radical copolymerization, within the experimental error, shows a similar compositional diagram. Furthermore, sequence distributions have been measured for living and conventional copolymers obtained at low conversions and no significant differences have been found. As in conventional copolymerization [202] sequence distributions of living copolymers correspond to predictions obtained from the penultimate model.

A new generation of nitroxides and alkoxyamines which are structurally different from TEMPO, such as 2,2,5-trimethyl-3-(1′-phenyletoxy)-4-phenyl-3-azahexane (**3**), overcome many of the problems typically associated with TEMPO based system [203,204]. One of the major advantages of these new initiators for SFRP is the ability to prepare a variety of statistical copolymers as well as decrease the temperature of polymerization below 100 °C.

Using **3** as initiator a wide variety of well-defined statistical copolymers of isoprene with styrenic and acrylate monomers have been prepared [204]. Independent of monomer feed composition, no changes in molecular weight control or polydispersity (1.1–1.2) have been observed [204].

3.3. Some examples of atom transfer statistical free-radical copolymerization

Many initiators, catalytic systems and reaction conditions have been used to obtain statistical copolymers via ATRP. As in copolymerization mediated by nitroxides the majority of research is devoted to study the control of molecular weight and MWDs and only in a few cases the monomer reactivity ratios or the studies of copolymerization rate have been performed. Furthermore, some NMR spectra of copolymers prepared via ATRP have been compared with those obtained by conventional free-radical copolymerization and a study of sequence distribution have been reported so far [205].

In this way, several research groups have carried out living/controlled free-radical copolymerization of methyl methacrylate (MMA) with butyl acrylate (BA). In some cases only one monomer molar fraction has been copolymerized. Uegaki et al. [206] have copolymerized MMA–BA using CCl_3Br/$NiBr_2(Pn\text{-}Bu_3)_2$/$Al(Oi\text{-}Pr)_3$ as initiating system, with 0.5 MMA molar fraction in the feed. These authors have found that the number average molecular weight increases with monomer conversion, agree well with the calculated values and have relatively narrow ($M_w/M_n = 1.3-1.5$) unimodal MWDs. In a similar way Moineau et al. [207] have investigated the statistical copolymerization of MMA–BA in toluene using ethyl 2-bromoisobutyrate and ethyl 2-bromopropionate catalyzed by $NiBr_2(PPh_3)_2$ as initiating systems. For an equimolar monomer feed composition, they found a linear dependence of $ln[M]_0/[M]$ versus time, a linear increase of the M_n with monomer conversion, but slightly higher than the theoretical values. Nevertheless the polydispersity is narrow. Moineau et al. [207] have also determined the monomer reactivity ratios at 85 °C from experiments at low conversion, resulting in values $r_{MMA} = 1.22$ and $r_{BA} = 0.35$.

The influence of monomer feed composition on the copolymerization rate of MMA–BA copolymerization is shown by Arehart and Matyjaszweski [208]. The copolymerization is carried out at 60 °C in bulk using methyl 2-bromopropionate/CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentametyldiethylentriamine (PMDETA) as initiating system. Copolymerization rate is higher for a 0.14 BA molar fraction in the feed than for a 0.84 BA molar fraction, which is contrary to the trend displayed in conventional free-radical copolymerization. M_n agrees well with the theoretical one at low conversions but deviates at conversions higher than 0.3. Furthermore, the polydispersity is relatively broad ($M_w/M_n > 1.45$). In addition they have found $r_{MMA} = 3.15$ and $r_{BA} = 0.37$ by application of the Meyer–Lowry equation [187]. Monomer reactivity ratios at 90 °C in ethyl acetate have also been determined by Matyjaszweski's group [209] using methyl 2-bromopropionate as initiator and CuBr/4,4′-di(5-nonyl)-2,2′-bipyridine (dNbpy) as catalyst. From experiments at high conversion and using the Kelen–Tudös method [188] the monomer reactivity ratios found were $r_{MMA} = 2.19 \pm 0.03$ and $r_{BA} = 0.39 \pm 0.1$. When the monomer reactivity ratios were calculated from the Jaacks method [210] their values were $r_{MMA} = 2.07 \pm 0.9$ and $r_{BA} = 0.35 \pm 0.12$.

In a very recent paper Ziegler and Matyjaszweski [186] describe the ATRP copolymerization of MMA and BA using methyl 2-bromopropionate as initiator and three different catalysts: CuBr/dNbpy, CuBr/PMDETA and CuBr/tris[2-(dimethylamino)ethyl]amine (Me_6TREN). Independent of the catalyst nature first order kinetics is observed until a certain conversion, which depends on the monomer feed composition, after which a curvature in the kinetic plot appears. Besides, the observed behavior of the copolymerization rate as a function of the monomer feed is dependent of the catalyst nature. Then, when CuBr/dNbpy or CuBr/Me_6TREN are used the copolymerization rate increases as the BA molar fraction monomer feed does, that is, copolymerization rate as a function of monomer feed composition presents the same behavior as in conventional free-radical copolymerization [46,97]. However, when CuBr/PMDETA is used, 0.14 and 0.53 molar fractions of BA in the monomer feed have similar copolymerization rates and a lower copolymerization rate is obtained for $f_{BA} = 0.84$. Furthermore, although copolymer molecular weight linearly increases with conversion, the lower polydispersities with the higher initiator efficiency are obtained when CuBr/dNbpy is used as catalyst. Monomer reactivity ratio values obtained when the copolymerization is performed using CuBr/dNbpy are different from those obtained when the catalytic system is CuBr/PMDETA, although joint confidence limits slightly overlap. In a comparative study between conventional and atom transfer copolymerization of MMA with BA, de la Fuente et al. [211] found that the ATRP copolymerization rate follows an opposite trend to that observed in conventional copolymerization when methyl 2-bromopropionate is used as inititor and CuCl/2,2′-bipyridine as catalyst.

Copolymerizations of S with BA have been carried out by Arehart and Matyjaszewski [212] at 100 °C using methyl 2-bromopropionate/CuBr/dNbpy as initiator system and by Chambard and Klumperman

[185] at 110 °C in xylene using tosylchloride (TsCl) as initiator and CuBr/di-4,4′-*n*-heptyl-2,2′-bipyridine (dHbpy) as catalyst. In both cases the monomer reactivity ratios are obtained from the Meyer–Lowry equation [187] using high and low molar fraction of S in the monomer feed, f_S. In a series of experiments Arehart and Matyjaszewski [212] combined high and low f_S and found values which are dependent on the experimental conditions. The determined values are in the interval $0.68 \le r_S \le 0.82$ and $0.22 \le r_{BA} \le 0.26$. However, Chambard and Klumperman [185] applied the Meyer–Lowry equation [187] for each experiment and found that at high f_S the r_S is well determined but the joint confidence interval indicate that r_{BA} contains a large error. When a low fraction of S is used in the monomer feed the situation is the opposite. The combination of experiments with high and low f_S allows to obtain monomer reactivity ratios values of $r_S = 0.87$ and $r_{BA} = 0.11$. The S monomer reactivity ratio compared well with that obtained by Arehart and Matyjaszewski [212] but the differences between reactivity ratio of BA are significant.

The influence of the activation/deactivation equilibrium reactions for both species (S and BA) on the resulting reactivity ratios have been evaluated by Chambard and Klumperman [185].

Arehart and Matyjaszewski [212] also studied the copolymerization kinetics and found that after a first linear period, a curvature appears, which points towards irreversible termination. The termination increases as the S content increases. The irreversible termination has been explained considering that as feed composition drift occurs due to the preferential consumption of one monomer (S), the deactivator concentration may change, resulting in a slower overall rate if the monomer left in the feed (BA) polymerizes under different equilibrium conditions. Taking into account that the equilibrium constant of S in homopolymerization is one order of magnitude higher than that of BA, more deactivator is generated in S polymerization, which may slow the consumption of BA during polymerization. This fact gives rise to nonlinear kinetics which are not due to irreversible destruction of end groups.

Copolymers of S/BA obtained by Arehart and Matyjaszewski [212] have M_n slightly higher than those theoretically expected, which can be due to inefficient initiation or to termination by combination, which is the chemical mechanism for termination of S and BA. However, copolymerizations performed at 100 and 70 °C do not show any temperature influence, which seem to indicate low initiation efficiency.

Copolymerization of S with MMA has been carried out by Kotani et al. [213]. Statistical copolymers with controlled composition and molecular weights have been obtained.

Copolymers of styrene with *N*-(2-acetoxyethyl) maleimide (AEMI) or S with *N*-phenylmaleimide (PhMI) have also been obtained by ATRP [214]. For both systems M_n linearly increases with conversion, matching the theoretically calculated values and having narrow MWDs. Furthermore, the copolymers of AEMI–S and PhMI–S obtained at low conversion by ATRP using different molar ratios of comonomers in the feed possess an alternating structure.

ATRP copolymerization of S with *N*-cyclohexylmaleimide (NCMI) have also been reported [215]. Monomer reactivity ratios have been determined and copolymers with predetermined molecular weights and polydispersities have been obtained.

A comparison between values of monomer reactivity ratios for methyl methacrylate–butyl methacrylate copolymerization using various living/controlled polymerization techniques have been reported by Haddleton et al. [216]. When ATRP and free-radical catalytic chain transfer (CCTA) are used the monomer reactivity ratios have similar values as those found in conventional free-radical copolymerization. From these results Haddleton et al. [216] suggested that ATRP and CCTA proceed via radical type of copolymerization.

The statistical copolymerization of vinyl monomers by ATRP is a new and important process, which allows synthesizing copolymers with low polydispersities and predetermined molecular weights. Furthermore, considering that monomer reactivity ratios normally have different values, spontaneous gradient copolymers can be prepared. It seems that composition and stereochemical structure of copolymer chains can be described by the MLTM. However, the copolymerization rate is dependent on the different equilibrium between dormant and actives species and more work must be done to know if the mechanism is similar or different to that of conventional copolymerization.

3.4. Some examples of statistical copolymers prepared using reversible addition fragmentation chain transfer

To the best of my knowledge the statistical copolymerization mediated by RAFT process has not been described in depth. However, Rizzardo's group [217] shows that a copolymer of S–AN obtained by thermal initiation in bulk at 100 °C in the presence of a dithioester has a polydispersity index of 1.07 after a polymerization time of 18 h. On the other hand, methyl methacrylate (MMA)–2-hydroxyethyl methacrylate (HEMA) [218] with a MMA fraction in the feed of 0.91 has been copolymerized at 60 °C in benzene using 2,2′-azobisisobutironitrile as initiator and a thiocarbonylthio compound as RAFT agent. After a polymerization time of 16 h a 75% conversion has been obtained and the copolymer has a polydispersity index of 1.21. The composition of copolymers (S–AN and MMA–HEMA) formed in presence of a thiocarbonylthio reagent is identical to those formed in its absence [219]. Rizzardo et al. [219] using an equimolar mixture of MMA and BA initiated the copolymerization at 60 °C with AIBN in the presence of a thiocarbonylthio compound and produced low polydispersity gradient MMA–BA copolymers.

De Brouwer et al. [220] have copolymerized styrene with maleic anhydride in an equimolecular feed composition using butyl acetate as a solvent, AIBN as initiator and two different RAFT agents. The first one is 2-cyanopro-2-yl dithiobenzoate (**a**) and the second one is a macromolecular RAFT agent obtained from hydroxyl-terminated ethylene butylene copolymer and a 2-cyaonopropyl-2-yl dithiobenzoate derivative (**b**). When **a** is used the molar mass of the copolymer is close to the expected theoretical value and polydispersity of the final product is 1.06. When **b** is used the polydispersity of the final product is 1.12.

Most of the chain transfer copolymerization studies have shown that overall copolymerization chain transfer constant follows the terminal model. However, there are some cases in which a penultimate effect has been claimed. Therefore, when copolymerization of two monomers is carried out in the presence of a RAFT agent it is necessary to elucidate not only the mechanism of transfer reactions but also how the chain transfer constant value for each monomer can affect the propagation step and the copolymerization rate.

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