Synthesis of Polymer Networks by "Living" Free Radical Polymerization and End-Linking Processes

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ABSTRACT: The synthesis of polymer networks by controlled free radical polymerization has been investigated in the case of atom transfer radical polymerization (ATRP). The synthesis of a difunctional initiator, bis(2-bromopropionyloxy) ethane (BBPE) makes possible the preparation of difunctional polymer precursors that can be used to prepare polymer networks by an end-linking process. The gels thus formed have been characterized by the determination of the fraction of polymer precursors unlinked to the cross-links and by the determination of the swelling equilibrium of the gels in xylene.

Introduction

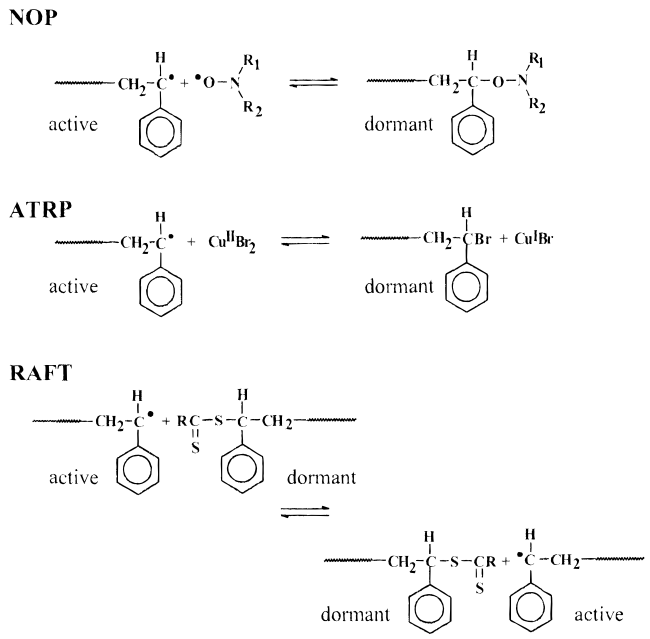
This paper deals with the synthesis of polymer networks by "living" free radical polymerization and end-linking processes. Two different aspects must be considered: (a) the "living" free radical polymerization methods and (b) the synthesis of polymer networks by end-linking processes.

Regarding point a, it is noted that some methods of controlling the free radical polymerization of vinylic monomers have already been published, for example: (i) nitroxide-controlled polymerization[1] (NOP), (ii) atom transfer radical polymerization[2] (ATRP), and (iii) degenerative chain transfer polymerization[3] (DCTP), which can be compared to the recent reversible addition fragmentation chain transfer polymerization[4] (RAFT). These methods are based upon some reversible reactions between the growing polymer radicals and "control" agents, leading to an exchange between "active" and "dormant" polymer species. Consequently, controlled reactions lead to the synthesis of well-defined polymers (cf. Scheme 1). In the case of NOP and ATRP, the reversible process also results in the decrease of the polymer radical concentration, with the resulting decrease of both the rate of termination reactions and the rate of polymerization.

The main interest of the considered methods is their ability to enable the synthesis of dormant "α,ω-difunctional" polymers, so-called "precursors", fitted at both ends by some potentially active moieties. These types of difunctional "dormant" polymers have already been used, both in ATRP[5] and RAFT[6] processes, as precursors for the synthesis of A−B−A block copolymers where B is the precursor. Such difunctional initiators have also been prepared in the case of nitroxide-controlled polymerization.[7]

Regarding point b, the conventional methods for the preparation of polymer networks involves either (i) free radical polymerization, (ii) polycondensation, or (iii) vulcanization (chemical or irradiation processes). In the conventional free radical process,[8] the cross-linking agent and the monomer are added to the reaction medium at the beginning of the polymerization. The cross-linking process results from the random copolymerization of the monomer and the cross-linking agent. The use of nitroxide and polymeric alkoxyamine to control such copolymerization has already been investigated.[9]

Scheme 1. Controlled Free Radical Polymerization Methods



These three conventional methods (including the nitroxide-controlled copolymerization) have no control of the network architecture parameter such as the molar mass or the polydispersity of the polymer chains between cross-links. Such control is only obtained by end-linking processes, i.e., reactions between α,ω-difunctional polymer precursors and cross-linking agents (cf. Scheme 2). Such end-linking processes have already been applied successfully, for example, (a) in the synthesis of polystyrene networks by living anionic polymerization[10] and (b) in the synthesis of poly(dimethylsil-

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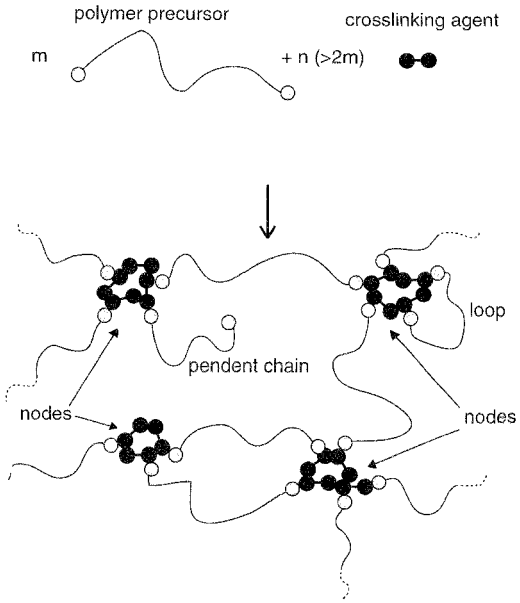
Scheme 2. Network Synthesis by an End-Linking Process



oxane) networks by hydrosilylation reactions between α,ω-dihydrogenopoly(dimethylsiloxane) and allylic cross-linking agents.[11] Both methods can control the cross-link functionality. A review dealing with the synthesis of such networks and the studies of their properties have been recently published.[12]

This paper deals with the use of the "living" character of "dormant" difunctional polymers in ATRP to prepare polymer networks by the end-linking process. The studies of NOP and RAFT systems will be published in subsequent papers.[13]

The following system has been investigated: (a) styrene (Sty) as the monomer, and (b) divinylbenzene (DVB) as the cross-linking agent. The preparation of the networks requires three steps: (i) the synthesis of some difunctional control agent, (ii) the polymerization of styrene in the presence of this control agent to prepare the "dormant" difunctional polystyrene, and (iii) the reaction of this difunctional polystyrene with DVB, leading to the network formation. In such a synthesis, the cross-links (nodes) are expected to be formed by the polymerization of the DVB initiated by the difunctional polymer as in the case of the anionic "living" difunctional polymers.

To investigate the structure of the networks thus formed, the fraction of unlinked polymer precursors (the "extractable" polymer) has been determined and studies have been made on the swelling equilibrium of the formed networks in xylene.

Experimental Section

Materials. Styrene (Aldrich) was treated with Na and distilled under vacuum. CuBr (98%, Aldrich) was purified following the conventional procedure.[14] 4,4′-Di-*n*-heptyl-2,2′-bipyridine (dHbipy) was prepared following the procedure described by Matyjaszewski et al.[15] The solvents (xylene, THF, toluene) were distilled *prior* to use. Divinylbenzene (Aldrich), 2,2′-bipyridine (Aldrich), anhydrous ethylene glycol (Acros, 99,8%), D,L-2-bromopropionic acid (Acros, 99%) and toluene-*p*-sulfonic acid (Aldrich) were used as received.

Instruments. ^{1}H NMR spectra were recorded in solution with a Bruker AM300 (300 MHz) spectrometer. ^{13}C NMR spectra were recorded at 75.5 MHz on a Bruker AM300 spectrometer, using the carbon signal of the solvent as the internal standard. Size exclusion chromatography (SEC) characterizations were carried out on a Waters chromatograph connected to a refractometer and a light-scattering detector (Wyatt) and calibrated with polystyrene standards. The light-scattering detector was used to characterize extractable polymers (see Discussion). THF was used as the solvent.

Synthesis. ATRP Initiator. Bis(2-bromopropionyloxy)-ethane (BBPE) is prepared as follows: to a 250 mL round-bottom flask equipped with a thermometer and a Dean−Stark apparatus containing a mixture of 0.7 g (3.7 mmol) of toluene-*p*-sulfonic acid and 77 g (0.5 mol) of 2-bromopropionic acid was added a mixture of 14 g (0.23 mol) of anhydrous ethylene glycol and 20 mL of toluene. The mixture was heated under reflux. The water and toluene thus formed were collected in the Dean−Stark apparatus. The reaction was conducted until no more water formation was observed. The product obtained (48 g, 0.21 mol, 94%) was recovered by distillation (bp = 90 °C, 0.01 bar). A synthesis of this compound starting from 2-bromopropionyl bromide has been published by Matyjaszewski et al.[16]

^{1}H NMR ($CDCl_3$): δ =4.39−4.42 (m, 4H, $-O-CH_2-CH_2-O-$), δ = 4.38 (q, 2H, CHBr), and δ = 1.82 (d, 6H, CH_3).

^{13}C NMR ($CDCl_3$): δ = 169.98 ($-COO$), δ = 63.1 ($-O-CH_2-CH_2-O-$), δ = 39.68 (CHBr), and δ = 21.59 (CH_3).

Polymer Precursors 1a−1g. A mixture of Sty:BBPE:CuBr:bipy, 100:1:2:6, was placed in a three-necked glass tube which was degassed by the freeze−pump−thaw process and then sealed under vacuum. The polymerization was conducted at 110 °C. The reaction was then stopped by freezing, and the solution was filtered through an aluminum oxide column. The polymer **1a** was recovered by two successive precipitations in methanol and was dried under vacuum at 50 °C to constant weight., Polymer precursors **1b**−**1g** were prepared following the same procedure by changing the polymerization time or the chemical nature and the concentration of the ligand (see Table 1).

The polymer precursor **1a** was used to check the difunctional character of BBPE (see Results and Discussion). Precursors **1b**−**1f** were used for the network syntheses. Precursor **1g** was used to study the cross-linking process and to check the occurrence of side reactions (see Results and Discussion).

Reactions 2b−2h. A solution of **1b**:CuBr:Dhbipy:DVB, 1:2:4:4, (1 g of **1b)** in 4 mL of xylene was placed in a siliconized (SUPELCO) glass tube. The tube was degassed by three freeze−pump−thaw cycles and then sealed under argon. The glass tube was placed in an oil bath at 110 °C for 80 h. The formed gel was recovered and placed in a large excess of xylene for 7 days in order to swell the gel and to extract the unlinked polymer. dHbipy was always used as the Cu ligand for the synthesis of these networks (the use of bipy does not lead to the formation of homogeneous networks, see Results and Discussion). Networks **2c**−**2g** were prepared following the same procedure by changing the ratio [precursor]/[DVB] (cf. Table 2). The reaction medium **2g** was sampled during the reaction in order to characterize the evolution of the reaction medium with time, before the gel point (samples **2g0**−**2g3**) and after the gel point (samples **2g4**−**2g9**). The samples obtained before the gel point were characterized by SEC. The samples obtained after the gel point were characterized by their swelling equilibrium ratios in the same manner as samples **2b**−**2f**.

The reaction medium **2h** corresponds to a system heated under the same experimental conditions as **2b** but in the absence of DVB. After 18 h this reaction medium has been injected into the SEC apparatus to determine the evolution of the molar mass of the polymer species. The result is given in Table 2 and Figure 4.

Determination of the Swelling Ratios. The determination of the swelling ratios were carried out by a method adapted from Peppas et al.[17] The following measurements were made on each sample: weight in air after reaction; weight in water after reaction; weight in air after swelling; weight in water after swelling; weight in air after drying. From these values, V_r, V_s , and V_p, the volumes of the gels before swelling, after swelling, and after drying, respectively, can be calculated.

Table 1. Experimental Conditions and Characterizations of Polymer Precursors

run	Cu ligand	Sty:BBPE:CuBr:ligand (mol:mol:mol:mol)	polym time (mn)	convn[a]	theor M_n[b] (g·mol^{-1})	exptl M_n[a] (g·mol^{-1})	polydispersity[a]
1a	bipy	100:1:2:6	270	0.70	7300	8700	1.5
1b	bipy	100:1:2:6	220	0.60	6200	6500	1.6
1c	bipy	100:1:2:6	120	0.28	2900	3700	1.5
1d	bipy	100:1:2:6	240	0.65	6700	7100	1.4
1e	dHbipy	100:1:2:4	140	0.36	3700	3500	1.2
1f	dHbipy	100:1:2:4	210	0.55	5700	5300	1.2
1g	bipy	100:1:2:6	150	0.41	4300	4700	1.3

[a] Determined by SEC (conversion: from peak area, M_w and M_n: from linear PS calibration). [b] Calculated from eq 1.

Table 2. Experimental Conditions for Polymer Network Syntheses and Characterization of Extractable Polymers

run	precursor	M_n precursor (g·mol^{-1})	concn (mol·L^{-1})	DVB:polymer (mol:mol)	extractable polymer (wt %)	M_n (M_w/M_n) of extractable polymer[a] (g·mol^{-1} × 10^{-3})
2b	**1b**	6500	0.038	4:1	12	55 (6.5)
2c	**1c**	3700	0.068	10:1	<1	90 (6.7)
2d	**1d**	7100	0.035	10:1	15	
2e	**1e**	3500	0.071	4:1	10	44 (7.3)
2f	**1f**	5300	0.047	10:1	6	130 (7.1)
2g9	**1g**	4700	0.053	10:1	5	see Table 3
2h	**1g**	4700	0.053	0:1	100 (soluble)	4.8 (1.3)

[a] Determined by SEC coupled with a light-scattering detector.

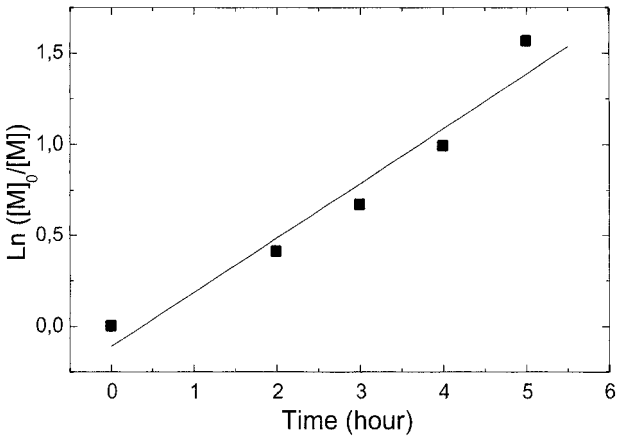


Figure 1. Kinetic plot of the bulk ATR polymerization of styrene at 110 °C. Sty:BBPE:CuBr:bipy = 100:1:2:6 (mol). Key: (■) experimental data; (line) linear fit.

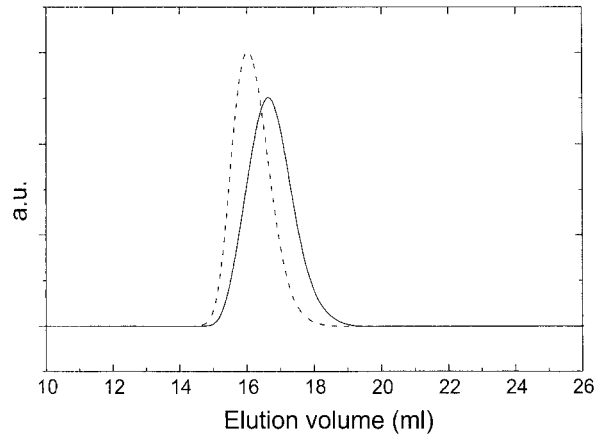


Figure 3. SEC traces for **1a.** Hydrolysis of the polystyrene precursor **1a**. Key: dashed line, before hydrolysis; solid line, after hydrolysis.

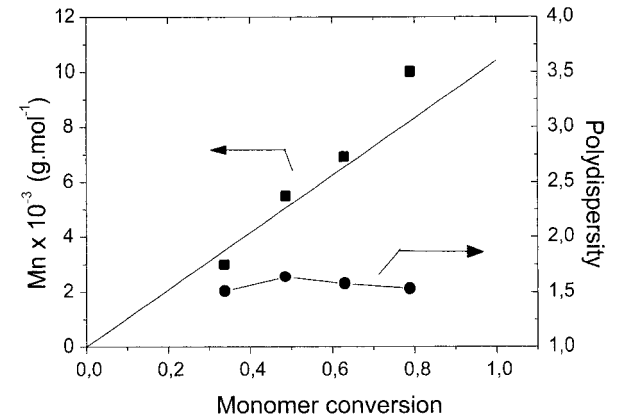


Figure 2. Variation of the molar mass and the polydispersity of polystyrene precursors vs the Conversion of the monomer in the ATR bulk polymerization of styrene at 110 °C. Sty: BBPE:CuBr:bipy = 100:1:2:6. Key: (■) M_n determined by SEC; (●) M_w/M_n determined by SEC; (straight line) theoretical curve calculated from eq 1.

The volume equilibrium ratio Q is defined as the ratio V_s/V_p. The volume fractions ϑ_r and ϑ_s are defined as $\vartheta_r = V_p/V_r$ and $\vartheta_s = V_p/V_s$ (= Q^{-1}), respectively.

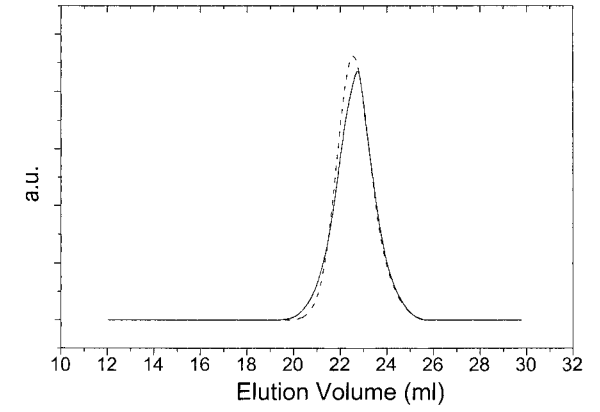


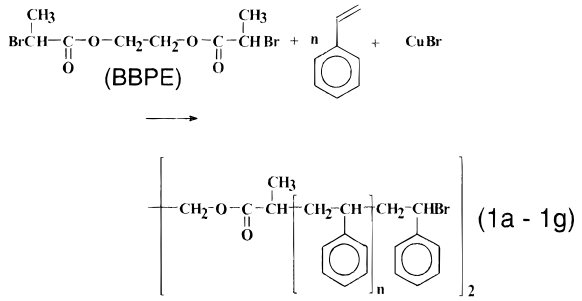
Figure 4. SEC traces for **1g.** Reaction in the absence of DVB (2 h). Key: dashed line, before reaction **2h**; solid line, after reaction **2h**.

Results and Discussion

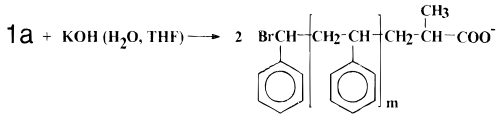
Synthesis of Polymer Precursors. The polymerization procedure was adapted from the standard procedures described by Matyjaszewski et al.[2b,15] The molar characteristics of the polymers obtained are reported in Table 1. As expected from the literature, the polymers

Scheme 3. Synthesis and Hydrolysis of Polymers Prepared with BBPE as the Initiator

Synthesis



Hydrolysis



prepared in the presence of dHbipy instead of bipy exhibit a lower polydispersity, attributed to a better solubility of the Cu complex[15].

To check the living character of the system, the polymerization of the following mixture Sty:BBPE:CuBr:bipy, 100:1:2:6, was studied. The recovered polymers at different reaction times were characterized by SEC (to determine both the monomer conversion and the molar mass average of the formed polymer). The variation of $\ln([Sty]_0/[Sty])$ is linear with time (cf. Figure 1), and the variation of the number average molar mass (M_n) with the monomer conversion is linear (cf. Figure 2), which is in agreement with eq 1

$$M_n = \frac{[\text{monomer}]}{[\text{initiator}]} \times \text{conversion} \times M_0 \qquad (1)$$

where M_0 is the molar mass of the monomer.

The polydispersity of the formed polymer is 1.5, which is a value compatible with the living character of the polymerization and the use of bipy as the Cu ligand. Using a monofunctional initiator and the same ligand, Matyjaszewski et al.[18] observed values ranging from of 1.1 to 1.5 for both styrene and methyl methacrylate.

As the initiator BBPE is difunctionnal, the formation of two polymer chains initiated by the two 2-bromopropionyoxy groups of the BBPE is expected. In the obtained polymer, these two chains are linked by the BBPE unit.

Similar results can be obtained by the use of other difunctional initiator such as α,α′-dibromo-*p*-xylene,[19] but in the case of BBPE, such a behavior can be examined by the hydrolysis of the ester bonds located in the BBPE unit (cf. Scheme 3). This type of hydrolysis has been carried out by heating the polymer **1a** to reflux in a THF:KOH/H_2O (0.25 mol·L^{-1}) mixture, 50:50 in volume, for 2 days. The medium is then neutralized with aqueous HCl (0.1 mol·L^{-1}). The molar characteristics (SEC characterization, cf. Figure 3) of the polymer before and after the hydrolysis are as follows: (a) before hydrolysis M_n = 8700 g·mol^{-1} and M_w/M_n = 1.50; (b) after hydrolysis M_n = 4570 g·mol^{-1} and M_w/M_n = 1.62. The decrease of the molar mass by a factor of 1.9 and the slight increase of the polydispersity are both compatible with the location of the BBPE unit near the center of the polymer chain.

Table 3. Evolution of the Reaction Medium 2g with Time

ref	time (min)	extractable polymer (wt %)	M_n[a] (g·mol^{-1})	M_w/M_n[a]	Q in xylene (25 °C)
2g0	0	(100)	4600	1.25	(soluble)
2g1	150	(100)	5460	1.5	(soluble)
2g2	210	(100)	6400	2.0	(soluble)
2g3	270	(100)	8000	6.0	(soluble)
		(gel point)			
2g4	660	27	6600	3.0	16.8
2g5	1410	20	5900	2.1	7.3
2g6	3160	19	5200	2.0	6.6
2g7	4200	12	5300	2.5	5.1
2g8	5280	6	4800	1.9	5.0
2g9	14400	5	5500	2.3	5.4

[a] Determined by SEC with linear PS calibration.

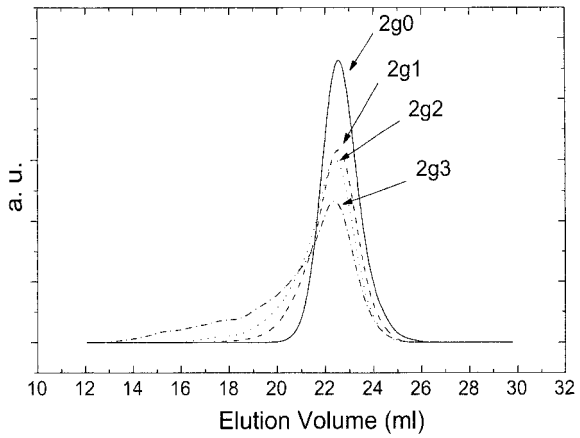


Figure 5. Evolution of the SEC traces with time for the reaction medium **2g.** Experimental conditions: see Table 2.

Synthesis of Polymer Networks. From experiment **2h**, it can be seen that in the absence of DVB, there is no significant evolution of the molar mass of the polymer precursor. From Figure 4, it can be observed that the SEC peaks corresponding to the precursor and to the polymer heated for 18 h in the presence of CuBr and dHbipy but in the absence of DVB are nearly identical. From this observation, it can be concluded that the rate of possible side reactions leading to a variation of the molar mass of the precursor such as the recombination of polymer radicals are slow enough to be neglected.

In the presence of DVB, the process leads to the formation of polymer networks. In all cases, the gel point is reached, even when the concentration of DVB is low, i.e., 2 DVB per chain-end (cf. Table 2).

Characterization of the Cross-Linking Process. The fact that the gel point is reached does not signify that the cross-linking process is quantitative in terms of the polymerization of vinylic functions located on DVB. Thus, the cross-linking process is expected to progress further, even after the gel point and despite the high ("infinite") viscosity of the reaction medium. Such a behavior has already been encountered[12] in the case of anionic syntheses of PS networks.

Before the gel point, the polymer species are completely soluble and can be characterized by SEC. After the gel point, the evolution of the reaction medium can be characterized by the determination of the swelling equilibrium ratio of the formed network. The results obtained for **2g** are reported in Table 3, Figure 5, and Figure 6.

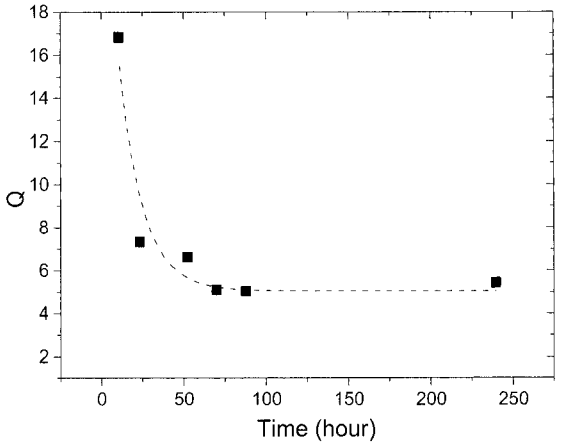


Figure 6. Variation of the equilibrium swelling ratio with time for reaction medium **2g.** Determined on network samples obtained after the gel point at different times.

As shown in Table 3, the swelling equilibrium ratio decreases rapidly after the gel point; i.e., the cross-linking density of the network increases. The cross-linking can be considered as "completed" after 80 h since there is no noticeable evolution of this parameter, whatever the yield of the DVB polymerization process. To achieve the network formation, the reaction media **2b**−**2f** have also been heated for 80 h.

Unlinked Polymer Chains in the Networks. This value may be experimentally determined by the fraction of polymer extracted from the networks in a good solvent. As a first approach, if p is the probability for one chain-end to be linked to nodes, then the fraction of unlinked polymer chains is $(1 - p)^2$, the fraction of polymer chains linked by only one chain end, i.e., the so-called "pendent" chains, is $2p(1 - p)$, and the fraction of polymer chains effectively connected to two nodes is p^2.

In most cases (cf. Table 2), the fraction of unlinked polymer is ca. 10%, (i.e. $p = 0.7$); therefore, the fraction of connective chains should be ca. 50%, and the fraction of pendent chains should be ca. 40%. From this calculation, it appears that the fraction of connective chains seems to be lower that observed in anionic processes which is generally[12] less than 5%, depending upon the molar mass of the precursor and the number of DVB per chain ends. However, the molar mass of the extractable polymers, determined by SEC coupled with a light-scattering detector (cf. Table 2), is, in all cases, much higher than the molar mass of the polymer precursor; i.e., these extractable polymer species are a mixture of unreacted (or nonfunctional) polymer precursors and hyperbranched structures. These polymer species remain totally soluble and cannot be removed from the solution by filtration.

Consequently, the determination of p, based on the weight fraction of extractable polymers, is largely underestimated. However, such high molar masses of extractable polymers are not expected (it is also very surprising to extract such high molar mass species from the network). It must be noted that the behavior of networks synthesized by reversible termination[13a] of RAFT processes[13b] is totally different, where the molar mass of the extractable polymer is similar to that of the polymer precursor.

From this discussion, it appears that the extractable polymers are to be considered as a mixture of unlinked hyperbranched structures and unlinked precursors. The heterogeneous composition of this mixture reflects perhaps some heterogeneity of the cross-linking process. The use of bipy as the ligand does not allow the formation of homogeneous gels, due to the low solubility of the Cu complexes: the formed network encapsulates the CuBr microparticles and the cross-linking process is stopped. The formed gels are optically heterogeneous. In the case of dHbipy, the solubility of Cu complexes is better and all the formed networks are optically homogeneous and transparent (but green tinted because of the presence of the Cu complex). However, the possibility cannot be excluded that there is some local microheterogeneity leading to the formation of branched structures chemically unlinked to the main network. Such a behavior has not been reported in the case of anionic synthesis of polymer networks.

Swelling Equilibrium of the Polymer Networks. To obtain the network structure, the polymer volume fraction in the swollen state ϑ_s and the polymer volume fraction in the gel after reaction but before swelling ϑ_r must be determined.[17] In a model network, the cross-linking density[20] ν corresponds to the number of "connective" polymer chains in the network, i.e., the number of polymer chains effectively linked at both ends to nodes and expressed in moles per unit volume of the dry network.

It has been found that[21]

$$\nu = \frac{\ln(1 - \vartheta_s) + \vartheta_s - \chi\vartheta_s^2}{\bar{V}(B\vartheta_s - A\vartheta_s^{1/3}h^{2/3})} \qquad (2)$$

In this equation, χ is the polymer solvent interaction parameter, h is the "memory" term and can be estimated as ϑ_r, and V is the molar volume of the solvent. A and B are factors depending on the theoretical model involved. Flory and Wall[22] have obtained $A = 1$ and $B = 2/f$, where f is the functionality of the nodes, i.e., the number of polymer chains connected to each cross-link. The value of χ was calculated from solubility parameters[23] (i.e., $\chi = 0.4$). A similar value may be obtained from Fujimoto et al.[24] in the case of polystyrene/toluene solution instead of polystyrene/xylene solution (however, the solubility parameters[23] of xylene and toluene are similar: 8.8 and 8.9, respectively).

In "ideal" networks, where all the polymer precursors are linked to nodes, the cross-linking density ν_i is

$$\nu_i = \frac{1}{M\vartheta_p} \qquad (3)$$

In this equation, ϑ_p is the specific volume of the polymer and M is the molar mass of the connective polymer chains, i.e., the molar mass of the polymer precursor. Thus, the theoretical cross-linking density can be calculated in the case of networks prepared by an end-linking process and compared to the experimental value determined by swelling experiments.

For each experiment, four different samples taken in the same network have been investigated in order to check the reproducibility of the experimental data, which can be related to the macroscopic homogeneity of the cross-linking process (cf. Table 4). In all cases, the networks are (green tinted) transparent polymeric materials and appear macroscopically homogeneous. However, with the exception of networks **2c** and **2g**, the experimental cross-linking density of the networks is lower than the ideal cross-linking density, whatever the

Table 4. Characterizations of Polymer Networks

sample	ϑ_r	ϑ_s	$\nu_{f=3}$[a] (mol·L^{-1} × 10^6)	$\nu_{f=\infty}$[b] (mol·L^{-1} × 10^6)	ν_i[c] (mol·L^{-1} × 10^6)
2b.1	0.152	0.071	74	44	
2b.2	0.237	0.084	67	45	
2b.3	0.224	0.085	74	48	
2b.4	0.176	0.080	83	50	
2b av	0.197	0.080	74	47	162
2c.1	0.211	0.192	688	258	
2c.2	0.230	0.214	849	310	
2c.3	0.231	0.197	646	258	
2c.4	0.220	0.203	774	285	
2c av	0.220	0.201	750	277	287
2d.1	0.230	0.093	88	56	
2d.2	0.202	0.085	81	51	
2d.3	0.210	0.081	70	45	
2d.4	0.195	0.088	92	56	
2d av	0.209	0.087	82	52	150
2e.1	0.198	0.091	97	59	
2e.2	0.202	0.092	99	60	
2e.3	0.202	0.094	104	62	
2e.4	0.211	0.098	109	65	
2e av	0.204	0.094	103	62	301
2f.1	0.200	0.097	112	62	
2f.2	0.190	0.103	137	69	
2f.3	0.215	0.098	107	64	
2f.4	0.212	0.097	105	62	
2f av	0.204	0.099	114	64	199
2g9.1	0.292	0.191	414	206	
2g9.2	0.340	0.171	252	146	
2g9.3	0.356	0.194	334	186	
2g9 av	0.329	0.185	325	177	234

[a] Theoretical cross-linking density of networks assuming three connective chains per node ($B = {}^2/_3$ in eq 2). [b] Theoretical cross-linking density of networks assuming an "infinite" number of connective chains per node ($B = 0$ in eq 2). [c] Ideal cross-linking density (eq 3).

number of connective chains per node. From the fraction of extractable polymer, this phenomenon can be attributed to some perturbation of the cross-linking process due to (a) some local heterogeneity of the system, (b) some defect of the polymer precursor (in terms of polymer functionality), or (c) the occurrence of some side reaction such as the thermal polymerization of the DVB (however, the concentration of the DVB seems to be too low to allow such a thermal polymerization).

Another tentative explanation could be the fact that the molar concentrations of the reaction media **2b**−**2g** are not identical, this could influence the rate of the overall process and therefore the yield of the cross-linking process.

In the case of networks **2c** and **2g9**, the extractable chain fraction is of the same magnitude as in the anionic process (<6%) and the cross-linking reaction may be assumed to be "complete". The value of the experimental cross-linking density (cf. Table 4) falls between the values expected for networks having nodes connected to three polymer chains (the highest possible value) $\nu_{f=3}$ ($B = {}^2/_3$ in eq 2) and networks having nodes connected to "infinite" number of polymer chains (the lowest possible value) $\nu_{f=\infty}$ ($B = 0$ in eq 2). In the obtained networks, the number of connective chains per node was estimated as approximately 30 and 6 for **2c** and **2g9**, respectively. The hydrolysis of the networks are being studied (in the same way as the hydrolysis of the precursors have been studied), which should enable the number of connective chains per nodes to be experimentally and directly determined.

Conclusion

As in the case of anionic living polymerization, the ATRP polymerization allows the synthesis of polymer networks by the end-linking process. The studies of the swelling equilibrium of different parts of the same sample shows that these gels are fairly homogeneous. However, the cross-linking density is often far below that of the theoretical value. The influence of various parameters such as (a) the polymeric precursor concentration, (b) the molar mass of the polymeric precursor, and (c) the molar concentration ratio [cross-linking agent]/[polymer precursor] are presently under investigation.

These techniques are expected to facilitate the preparation of a wide range of "model" networks, where the chemical structure of the connecting chains can range from homopolymers and mixtures of homopolymers to architecturally controlled polymers[13a] such as block copolymers, gradient copolymers, stars, etc., i.e., all the polymer structures which can be obtained by "living" free radical polymerization.

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