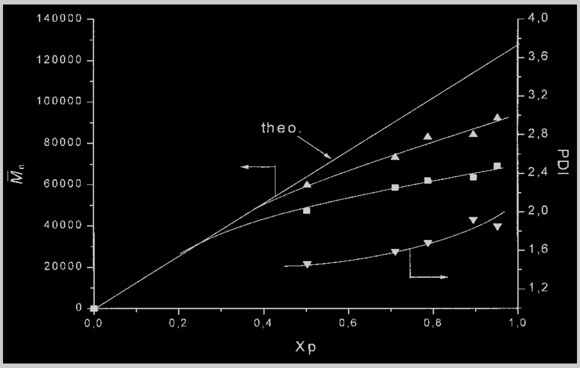
Communication: Poly(butyl acrylate) (PBuA) of high molecular weight was synthesized by atom transfer radical polymerization (ATRP) in ethyl acetate. Whereas for low molecular weight polymers, a linear increase of the number-average molecular weight, $\overline{M}_n$, versus conversion and narrow molecular weight distributions indicate the suppression of side reactions, a downward curvature in the plot of $\overline{M}_n$ versus conversion was observed for high molecular weights ($\overline{M}_n > 50\,000$). This effect is explained by chain transfer reactions, leading to branched polymers. GPC measurements with a viscosity detector give evidence for the branched structure of high molecular weight polymers obtained in ATRP. In addition, transfer to solvent or monomer is likely to occur.



Number-average molecular weights determined by GPC using linear PBuA standards (■) or universal calibration (▼), as well as polydispersity index (▲) versus conversion for the time conversion plot in Fig. 3

Evidence for chain transfer in the atom transfer radical polymerization of butyl acrylate

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Introduction

Radical polymerization is one of the most important commercial processes leading to high molecular weight polymers because a wide variety of monomers can be polymerized and copolymerized. This process does not demand a high level of purity, such as required by anionic polymerization. A drawback of conventional radical polymerization is the lack of control of the molecular weight and its distribution due to the presence of unavoidable chain-breaking reactions, such as termination or transfer. Various strategies have been developed recently in order to minimize termination reactions and thus, to reach a controlled radical polymerization[1–3]. One approach is atom transfer radical polymerization (ATRP). Dormant halogenated chain-ends are reversibly activated by a copper (I) complex, $\mathrm{CuX/L_n}$ (X = Cl or Br, L = ligand, n = 1 or 2) via halogen atom transfer reaction leading to free radicals and Cu(II) complexes in a fast, dynamic equilibrium. For the polymerization of methacrylates and acrylates, *p*-toluenesulfonylchloride[4], *α*-bromo- and chloroesters[3,5] have been used as initiators. Homogeneous polymerization is reached by using 4,4′-dinonyl-2,2′-bipyridine (dNbipy) as ligand resulting in PMMA of low polydispersity (PDI < 1.05) and molecular weights up to 10^5 (ref.[6]). New ligands, such as *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) show an acceleration of the rate of polymerization due to the lower redox potential of the coordination complex between copper and aliphatic oligoamines[7].

Formerly, we had synthesized graft copolymers with an acrylate backbone, e.g. PBuA-*graft*-PMMA, via conventional radical copolymerization of PMMA macromonomers with BuA[8]. For applications as thermoplastic elastomers, high molecular weight copolymers are needed corresponding to a high degree of polymerization of the backbone ($\overline{DP}_n \approx 1000$). In order to gain better control of the chain length of the backbone we have investigated the use of ATRP for this copolymerization[9]. Here we wish to report experiments of polymerization of BuA up to high molecular weights which indicate that transfer cannot be excluded in this process.

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Experimental part

Reagents

Butyl acrylate (BuA, BASF AG) was fractionated from CaH_2 over a 1 m column filled with Sulzer packing at 45 mbar, stirred over CaH_2, degassed and distilled in high vacuum. CuBr (95%, Aldrich) was purified by stirring overnight in acetic acid. After filtration it was washed with ethanol, ether, and then dried. *N,N,N′,N″N″*-pentamethyldiethylenetriamine (PMDETA, Aldrich) was degassed and distilled in high vacuum. Ethyl acetate (Aldrich), copper powder (99% for organic synthesis, Aldrich) and methyl 2-bromopropionate (Aldrich) were used as received.

Polymerization

All solid chemicals were weighed into an ampoule and degassed. In a glove-box, all degassed liquids were added to the ampoule which was sealed and immersed in an oil bath at 90 °C. Experiments were performed with CuBr as catalyst and methyl 2-bromopropionate (MBP) as initiator in ethyl acetate as solvent. All kinetic samples were taken from the same ampoule by cooling down to room temperature in a glove-box, withdrawing an aliquot, and placing the ampoule back into the oil bath. After the reaction, the solution was diluted with THF and filtered over an aluminium oxide column in order to remove the catalyst. After evaporation of the solvent, the polymer was dissolved in benzene, filtered and freeze-dried.

Analysis

Monomer conversion was determined from the reaction solution by GC. Decane was used as internal standard. GPC was performed using THF as eluent at a flow rate of 1 ml/min. Detectors: 2 × Jasco-Uvidec 100 III with variable wavelength, Bischoff RI detector 8110, Viscotek H 502 B and column sets: (a) 2 × 60 cm, 5 μ PSS SDV gel, 100 Å and linear: 10^2–10^5 Å; (b) 3 × 30 cm, 5 μ PSS SDV gel, 10^3 Å, 10^5 Å and 10^6 Å. PMMA and PBuA standards obtained by anionic polymerization were used for calibration of column set (a) and universal calibration in conjunction with the viscosity detector was used for column set (b). The absolute molecular weights of the PBuA standards were determined by MALDI-TOF mass spectrometry and light scattering measurements$^{10)}$.

Results and discussion

All polymerizations of BuA were performed in ethyl acetate at 80 °C using methyl α-bromopropionate (MBP) as initiator and CuBr/PMDETA as catalyst. The initial monomer concentration was $[BuA]_0$ = 2.33 mol/l. The kinetic plots for a calculated final degree of polymerization, $\overline{DP}_n$ = 100, are presented in Fig. 1 and 2. A linear first-order time-conversion plot is observed indicating a constant number of growing radicals. The number-average molecular weights of the polymers increase linearly with conversion and are close to the calculated values (Fig. 1 and 2). The polydispersity index first decreases with conversion and then remains at low values ($\overline{M}_w/\overline{M}_n$ = 1.15). These results show that termination and transfer reactions are insignificant at low molecular weights.

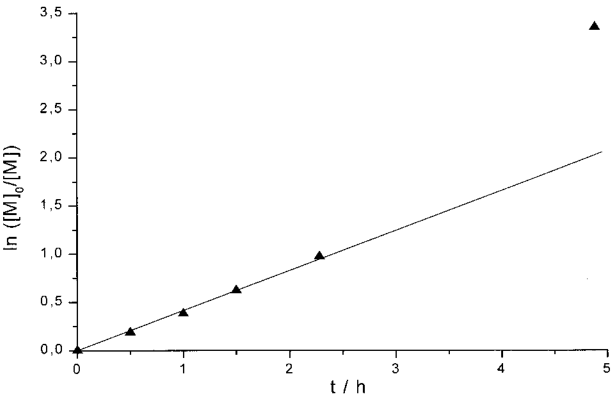

Fig. 1. First-order time-conversion plot of the ATRP of BuA in ethyl acetate at 80 °C. $[BuA]_0 : [MBP]_0 : [CuBr]_0 : [PMDETA]$ = 100 : 1 : 2 : 2

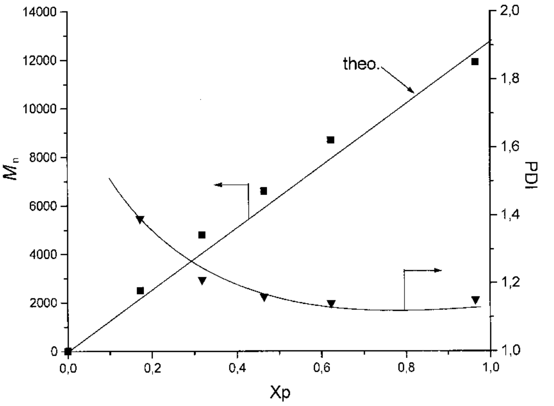

Fig. 2. Number-average molecular weight and polydispersity index versus conversion for the time-conversion plot in Fig. 6

In the next experiment, the concentration of the initiator was reduced by a factor of 10 in order to obtain higher molecular weights ($\overline{DP}_n$ = 1 000). In order to increase the polymerization rate, copper powder was added. Cu(0) transforms Cu(II) (formed during termination events) back to Cu(I)$^{11)}$. Now, the first-order time-conversion plot (Fig. 3) shows a distinct downward curvature. This is easily explained by some termination reactions leading to an increase in the concentration of Cu(II) shifting the activation equilibrium toward the dormant side, since $R_p \propto [Cu(I)]/[Cu(II)]^{11)}$.

A downward curvature is also observed in the plot of $\overline{M}_n$ (as determined by GPC using linear PBuA standards) versus conversion (Fig. 4), and the polydispersity index increases with conversion up to a value of $\overline{M}_w/\overline{M}_n \approx 1.9$. Termination by recombination would rather lead to an upward curvature of the plot of $\overline{M}_n$ vs conversion and a polydispersity of 1.5. Thus, a reasonable explanation could be chain transfer.

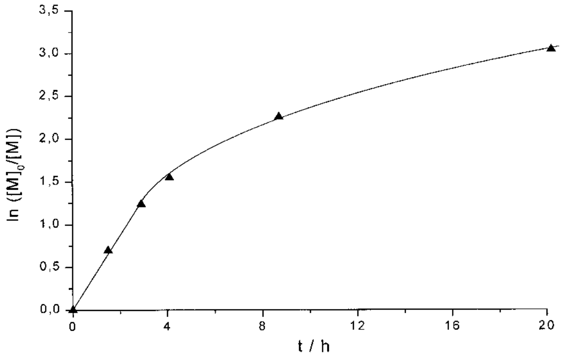

Fig. 3. First-order time-conversion plot of the polymerization of BuA in ethyl acetate at 80 °C. $[BuA]_0 : [MBP]_0 : [CuBr]_0 : [PMDETA] : [Cu]_0 = 1000 : 1 : 2 : 2 : 2$

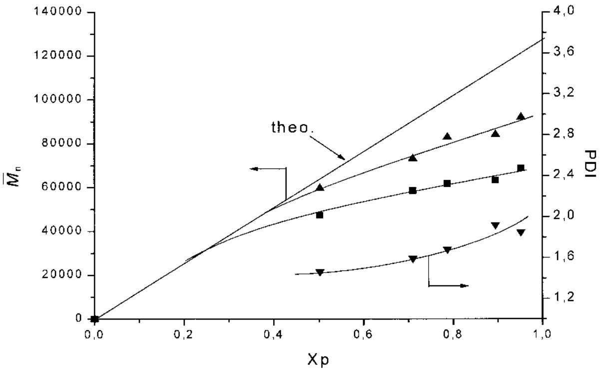

Fig. 4. Number-average molecular weights determined by GPC using linear PBuA standards (■) or universal calibration (▼), as well as polydispersity index (▲) versus conversion for the time conversion plot in Fig. 3

When $\overline{M}_n$ is determined by using a viscosity detector and universal calibration[12)], the downward curvature is less pronounced. Since branched polymers have a lower hydrodynamic volume than linear ones, the polymers will elute later in GPC leading to an apparently lower $\overline{M}_n$ value. GPC separates according to the hydrodynamic volume, thus the product of intrinsic viscosity and molecular weight of branched structures equals to that of linear ones at a given elution volume ($V_h = [\eta]_{br} \cdot M_{br} = [\eta]_{lin} \cdot M_{lin}$). Thus, molecular weights determined by GPC using a viscosity detector are not affected by branching, in contrast to values determined from calibration with linear standards. The observed deviation of $\overline{M}_n$ values thus indicates the existence of branched structures.

This is further corroborated by Mark-Houwink plots obtained from on-line viscosity measurements of PBuA samples at different conversions (Fig. 5). At a given molecular weight, the intrinsic viscosity is lower for polymers obtained at higher conversions. The Mark-Houwink parameter of the higher molecular weight sample (95% conversion), $a = 0.62 \pm 0.02$, is significantly lower than that obtained at 50% conversion ($a = 0.67 \pm 0.01$), and

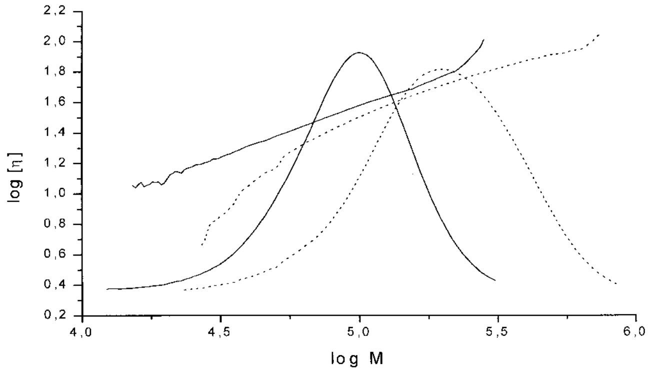

Fig. 5. Mark-Houwink plots of PBuA samples with corresponding molecular weight distributions synthesized by ATRP at 50% conversion (———), $a = 0.67 \pm 0.01$, and at 95% conversion (· · ·), $a = 0.62 \pm 0.02$

this value is again lower than that of linear PBuA standards made by anionic polymerization[10)] ($a = 0.716$) indicating an increasingly branched structure. The contraction factor, $g' = [\eta]_{branched}/[\eta]_{linear}$, steadily decreases with increasing molecular weight.

The existence of branched structures can be explained by transfer to polymer. Recently, Ahmad et al.[13)] gave NMR evidence for transfer to polymer in the conventional radical polymerization of BuA. The transfer constant has not been determined so far, since it is a complicated function of monomer concentration and conversion. Transfer to polymer should not effect $\overline{M}_n$, since the total number of chains remains constant.

The residual downward curvature of $\overline{M}_n$ obtained by universal calibration compared to the theoretical line could be explained by transfer reactions to solvent, ethyl acetate, or monomer BuA. In principle, the transfer constant of the monomer ($k_{tr,M}/k_p = 2 \times 10^{-5}$ at 90 °C[14)]; $k_{tr,M}/k_p = 8 \times 10^{-5}$ at 70 °C[15)]) is too low to affect the molecular weight so strongly. The transfer constant of ethyl acetate has not been determined so far, but it should be lower than that of ethyl propionate ($k_{tr,S}/k_p = 2.6 \times 10^{-4}$ at 90 °C[14)]) because ethyl acetate lacks secondary protons.

Conclusions

GPC-viscosity coupling gives good evidence for the existence of chain transfer in the ATRP of butyl acrylate at high molecular weights. From the mechanism of controlled radical polymerization it becomes clear that transfer reactions cannot be suppressed. The main principle of termination control is the decrease in free radical concentration which decreases the probability of radical encounters necessary for recombination or disproportionation, $R_t/R_p \propto [P^\bullet]/[M]$. However, no effect is expected on the probability of a given radical to undergo transfer which is given by the ratio of concentration of the transfer agent,

[TA], to monomer and, thus, independent of the radical concentration, $R_{tr}/R_p = k_{tr}[TA]/k_p[M]$. Since the propagating species is still a free radical, its selectivity, k_p/k_{tr} should remain unchanged. Similarly, it will be difficult to polymerize monomers which are liable to monomer transfer (due to tertiary hydrogens, e.g. 2-ethylhexyl acrylate) to high molecular weights. Polymerizations should be performed at lower temperature since the energy of activation for transfer is higher than that for polymerization ($E_{a,tr} > E_{a,p}$).

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