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Synthesis of Polymers Containing Cross-Linkable Groups by Atom Transfer Radical Polymerization: Poly(allyl methacrylate) and Copolymers of Allyl Methacrylate and Styrene

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ABSTRACT: Poly(allyl methacrylate) (PAMA) and random copolymers of styrene (St) with allyl methacrylate (AMA) were prepared via atom transfer radical polymerization. For the homopolymerization of AMA, the maximum conversion depends on the reaction conditions and on the monomer/initiator ratio. For the copolymerization, AMA conversions of up to 90% were obtained while no cross-linking occurred. Kinetic studies of the homopolymerization revealed a controlled polymerization up to a certain conversion whereas at higher conversions, multimodal molecular weight distributions caused by branching reactions and cross-linking were observed. The copolymerization of AMA with St allowed a controlled reaction up to conversions higher than 90%. The copolymers obtained were soluble in standard organic solvents. In a subsequent reaction, these copolymers were cross-linked both thermally and photochemically using suitable initiators. Moreover, pendant double bonds were brominated quantitatively.

Introduction

Monomers containing two reactive double bonds are commonly used as cross-linking agents, e.g., divinylbenzene, ethylene glycol dimethacrylate (EDMA), or diethylene glycol dimethacrylate (DegDMA). Because of their symmetric structure, both double bonds exhibit equal chemical reactivity. In contrast, monomers containing two double bonds of different reactivities may result in regioselective reactions. Allyl methacrylate (AMA), though frequently used as a cross-linker, belongs to this class of monomers since it contains both a methacrylic and an allylic double bond.

AMA is considered to be a tetrafunctional monomer since during radical polymerization not only the addition of the chain end radical to both kinds of double bonds but also a cyclization reaction of both addition products to yield five- and six-membered lactone rings appears to be possible.[1,2] Though cyclization reactions have been investigated and discussed,[3] more recent studies involving NMR spectroscopy did not reveal any indication of the formation of in-chain lactone rings.[4] To estimate the reactivity ratios of methacrylic and allylic double bonds in free radical polymerization, NMR studies—mainly on model compounds preventing cross-linking reactions—were carried out, indicating that conversion of the allylic double bond only becomes significant when conversion of both vinylic/acrylic double bonds (i.e., the methacrylic double bond of AMA and double bonds of comonomers like methyl methacrylate, *n*-butyl acrylate, styrene) is very high.[4] Despite a very low molar ratio of methacrylic to allylic double bonds in the polymer, the methacrylic double bonds contributed significantly to branching and cross-linking reactions, based on theoretical predictions[4] that have been contradicted by Matsumoto;[5,6] the experimental evidence, however, cited for this contradiction (^{1}H NMR, ^{13}C NMR, IR) is also consistent with formation of pendant methacryloyl groups in a quantity below the detection sensitivity of the analytical methods.

Because of the nature of free radical polymerization, cross-linking involving AMA is inevitable even at the early stages of the reaction. To achieve higher conversions before cross-linking and gel formation, Cohen and Sparrow pointed out two possible ways:[7] (1) During the early stages, the reactivity of the less reactive group (i.e., the allyl group) has to be decreased; despite this decrease, the less reactive group still has to be able to react during later reaction stages (i.e., at the time cross-linking is supposed to occur). (2) During the early stages, gelation (cross-linking) has to be prevented by diminishing the chain length. The latter is achieved by the application of chain transfer agents.[7] In studies concerning AMA homo-[5] and copolymerization,[6] Matsumoto and co-workers applied lauryl mercaptan as a chain transfer agent. Furthermore, these authors pointed out that at higher conversion intermolecular cross-linking processes are enhanced by the entanglement of polymer chains.[5] Alternatively, radical polymerization of AMA as a comonomer is often carried out as an emulsion polymerization to overcome the disadvantages of cross-linking reactions.[8−10] For a copolymerization, the cross-linked latex particles obtained are inhomogeneous due to different solubility of the comonomers in the water phase; therefore, core−shell particles are formed.

We considered it to be desirable to have access to non-cross-linked and thus soluble polymers containing pendant double bonds. Such a polymer would offer the possibility to undergo the cross-linking reaction on demand (e.g., by irradiation or thermal treatment). The non-cross-linked starting material could be processed in solution, which seems to be a feasible approach for coatings as well as for the preparation of interpenetrating or semiinterpenetrating polymer networks.

To the best of our knowledge, the living/controlled polymerization of AMA forming linear polymer chains with pendant allyl groups has only been carried out by

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an anionic mechanism.[11] However, the homopolymer prepared (poly(allyl methacrylate), PAMA) undergoes a relatively fast cross-linking reaction on standing in air even at room temperature. Therefore, copolymers of AMA that contain pendant double bonds in much lower concentration seem to be more suitable for application. Unfortunately, copolymerization of AMA with styrene (St) and methyl methacrylate (MMA) via the anionic route leads to unsatisfactory results because of unfavorable copolymerization parameters (in the copolymerization of AMA and St, PAMA with only a few repeating units of St is obtained, whereas in the copolymerization of AMA and MMA, MMA is preferentially incorporated into the polymer chain).[11] A synthetic route that allows the variation of AMA repeating units within a larger range is thus needed. Radical polymerization could be such an alternative as long as certain conditions are fulfilled: Cohen's and Sparrow's demand for diminishing the chain length[7] can be matched without the addition of chain transfer agents if all radical chains are started at the same time and constantly grow with the same rate. Controlled radical polymerization appears to be most suitable for this purpose. Among controlled radical polymerization techniques, atom transfer radical polymerization (ATRP)[12−14] has become a powerful tool that has been used for the synthesis of complex architectures.[15−17]

In this paper, the successful synthesis of poly(allyl methacrylate) and a copolymer of St and AMA via ATRP is reported. Our aim was the synthesis of a soluble polymer that can afterward be cross-linked on demand. Special emphasis was placed on kinetic studies which allow a detection of side reactions occurring during ATRP in the presence of allyl methacrylate.

Experimental Part

Materials. Styrene (99%, Aldrich) and allyl methacrylate (98%, Aldrich) were purified via column chromatography over Al_2O_3 (Fluka, type 5016A basic). 2,2′-Azobis(2-methylpropionitrile) (AIBN, 98%, Acros), (1-bromoethyl)benzene (PEBr, 97%, Avocado), *p*-fluorophenylsulfonyl chloride (FPSC, 98%, Aldrich), CuCl (>97%, Lancaster), CuBr (98%, Aldrich), 2,2′-bipyridine (Bpy, 99%, Avocado), pentamethyldiethylenetriamine (PMDETA, >98%, Merck), *n*-butyl acetate (BuAc, >98%, Merck), bromine (>99%, Fluka), 2,2-dimethoxy-2-phenylacetophenone (99%, Aldrich), and dichloromethane (>99.5%, Roth) were used without further purification. Bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (Irgacure 819) was a donation of Ciba Specialty Chemicals. All other chemicals were used as received.

All reactions were carried out in a nitrogen atmosphere. Nitrogen (Linde, 5.0) was passed over molecular sieves (4 Å) and finely distributed potassium on aluminum oxide.

Measurements. ^1H NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer at 300 MHz. Deuterated chloroform ($CDCl_3$) was used as a solvent, and tetramethylsilane (TMS) served as an internal standard.

Gel permeation chromatography (GPC) analyses were carried out using a high-temperature GPC device at 80 °C (Polymer Laboratories PL-GPC210 with a Bischoff HPLC compact pump) and a refractive index detector (Polymer Laboratories). The eluting solvent was *N*,*N*-dimethylacetamide (DMAc) with 2.44 g/L LiCl and a flow rate of 0.8 mL/min. The combination of DMAc as a solvent and elevated temperatures was chosen because solubility of small residues of Cu complexes included in the polymer samples is assured; we made the experience that GPC of ATRP samples in more common solvents (e.g., THF) at room temperature led to problems (e.g., plugged inline filters). Four columns with MZ-DVB gel were applied: length of each column 300 mm, diameter 8 mm, diameter of gel particles 5 μm, nominal pore width 100, 100, 1000, and 10000 Å. Calibration was achieved using polystyrene standards. The molecular weights determined are not absolute values, but "polystyrene equivalents".

GC measurements were performed on a Siemens Sichromat 1-4 gas chromatograph equipped with an FID using a Hewlett-Packard PONA column (cross-linked methylsiloxane, HP part no. 19091S-001, length 50 m, diameter 0.2 mm, film thickness 0.5 μm, carrier gas N_2). The injector and detector temperatures applied were 200 and 300 °C, respectively. The temperature program employed was 50−250 °C, 5 min isothermal, heating at 8 K/min. BuAc used as a solvent in the polymerization served as the internal standard (correction factor for styrene 0.52, for AMA 0.86). Conversions were calculated by observation of the decrease of the monomer peak area relative to the standard peak area.

UV spectra were recorded on a Shimadzu UV-160A at room temperature (solvent: distilled THF).

General Procedure for AMA Homo- and Copolymerization via ATRP. In a typical homopolymerization procedure, *p*-fluorophenylsulfonyl chloride (0.20 g, 1 mmol), CuCl (0.10 g, 1 mmol), PMDETA (0.21 g, 1.2 mmol), and AMA (6.31 g, 50 mmol) were stirred in BuAc (6 mL). Reaction was started by immersion into an oil bath (110 °C). After 25 min the mixture was rapidly cooled to room temperature and quenched by addition of CH_2Cl_2 (10 mL) followed by stirring in air until the copper complex was completely oxidized. The copper complex was removed by repeated stirring with aluminum oxide and subsequent filtration. The polymer was precipitated in cold pentane. To prevent cross-linking of the homopolymer, the sample has to be stabilized and stored under nitrogen. Yield: 1.04 g (16%), $M_{n,GPC} = 7300$, $M_w/M_n = 1.48$. ^1H NMR: $\delta = 0.88/1.04/1.26$ (*rr*/*mr*/*mm*, s, 3H, CH_3), 1.73−2.17 (broad signal, 2H, CH_2-backbone), 4.48 (s, 2H, OCH_2), 5.25 (d, 1H, $CHCH_2$-allyl), 5.34 (d, 1H, $CHCH_2$-allyl), 5.78−6.03 ppm (broad signal, 1H, $CHCH_2$-allyl).

In a typical copolymerization procedure, (1-bromoethyl)benzene (0.19 g, 1 mmol), CuBr (0.14 g, 1 mmol), PMDETA (0.21 g, 1.2 mmol), St (4.69 g, 45 mmol), and AMA (0.63 g, 5 mmol) were stirred in BuAc (5 mL). Reaction was started by immersion into an oil bath (110 °C). After 20 h the mixture was rapidly cooled to room temperature and quenched by addition of CH_2Cl_2 (10 mL) followed by stirring in air until the copper complex was completely oxidized. The copper complex was removed by repeated stirring with aluminum oxide and subsequent filtration. The polymer was precipitated in methanol. Yield: 4.67 g (84%), $M_{n,GPC} = 18\,200$, $M_w/M_n = 10.10$. ^1H NMR: (i) St repeating units: $\delta = 1.0{-}2.6$ (broad signal, 3H, CH_2 and CH, backbone), 6.2−7.5 ppm (broad signal, 5H, aromatic H); (ii) AMA repeating units: $\delta = 0.3{-}1.0$ (broad signal, 3H, CH_3), 1.0−2.6 (broad signal, 2H, CH_2-backbone), 3.2−4.6 (broad signal, 2H, OCH_2), 4.7−5.3 (broad signal, 1H, $CHCH_2$-allyl), 5.3−6.0 ppm (broad signal, 2H, $CHCH_2$-allyl).

If Bpy was used as a ligand, the copper complex was removed by filtration and extraction with 5% HCl.

Kinetic Studies of AMA Homopolymerization. Kinetic studies were carried out analogously to the general polymerization procedure. During the reaction time, samples of ca. 1 mL were withdrawn, dissolved in $CDCl_3$ (1 mL), and cooled in an ice bath. Afterward, the solution was filtered through Al_2O_3. The conversion was determined by ^1H NMR spectroscopy comparing the integrals of the monomer and polymer OCH_2 protons (at 4.65 and 4.48 ppm, respectively); M_n was determined by means of GPC.

Kinetic Studies of St/AMA Copolymerization. Kinetic studies were carried out analogously to the general polymerization procedure. During the reaction time, samples of ca. 1 mL were withdrawn, dissolved in CH_2Cl_2 (1 mL), and cooled in an ice bath. Afterward, the solution was filtered through Al_2O_3. The conversions and M_n were determined by GC and GPC, respectively.

Bromination of Pendant Double Bonds. A St/AMA copolymer (0.50 g; $M_{n,GPC} = 8700$, $M_w/M_n = 1.62$, content of AMA repeating units: 20 mol %) was dissolved in CH_2Cl_2 (5 mL). The solution was cooled to 0 °C, and Br_2 (0.16 g, 1 mmol), dissolved in CH_2Cl_2 (3 mL), was added. The mixture was stirred at 0 °C for 45 min and afterward stored at 4 °C in darkness for 48 h. The polymer was precipitated in methanol. Yield: 0.45 g (90%) of quantitatively brominated (according to ^{1}H NMR spectrum) copolymer ($M_{n,GPC} = 10\,800$, $M_w/M_n = 1.65$). Yield: 4.67 g (84%), $M_{n,GPC} = 18\,200$, $M_w/M_n = 10.10$. ^{1}H NMR: (i) St repeating units: $\delta = 1.0-2.6$ (broad signal, 3H, CH_2 and CH, backbone), 6.2−7.5 ppm (broad signal, 5H, aromatic H); (ii) 2,3-dibromopropyl methacrylate repeating units: $\delta = 0.3-1.0$ (broad signal, 3H, CH_3), 1.0−2.6 (broad signal, 2H, CH_2-backbone), 2.6−4.7 ppm (broad signal, 5H, CH_2Br, CHBr, OCH_2).

Cross-Linking Reactions. Thermal cross-linking was achieved using AIBN as the initiator. For the photochemical cross-linking procedure, bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (= Ciba Irgacure 819), a BAPO (bisacylphosphine oxide)-type initiator, was applied. In a typical procedure for thermal cross-linking, P(St-*co*-AMA) (201 mg, $M_{n,GPC} = 4700$, $M_w/M_n = 1.28$) and AIBN (10 mg, 5 wt %) were dissolved in CH_2Cl_2. To prepare a film, the solvent was evaporated and the polymer/initiator mixture was dried in vacuo. Samples were placed in an oven at 100 °C for 24 h. After these procedures, CH_2Cl_2 was added and the samples were left in darkness at room temperature for 12 h before removal of the soluble part. The CH_2Cl_2 phase containing the soluble non-cross-linked fraction of the polymer was then removed, dried under reduced pressure, and analyzed by means of GPC ($M_{n,GPC} = 5500$, $M_w/M_n = 14.26$). The insoluble residue was dried in vacuo and weighed (83 mg).

Film preparation was analogous in a typical photo-cross-linking procedure. Samples were irradiated for 3.5 h using an Osram Ultra-Vitalux 300 W UV lamp at a distance of 10 cm.

To estimate the extent of cross-linking, the weight of the insoluble product was compared with the initial weight in all cases.

Results and Discussion

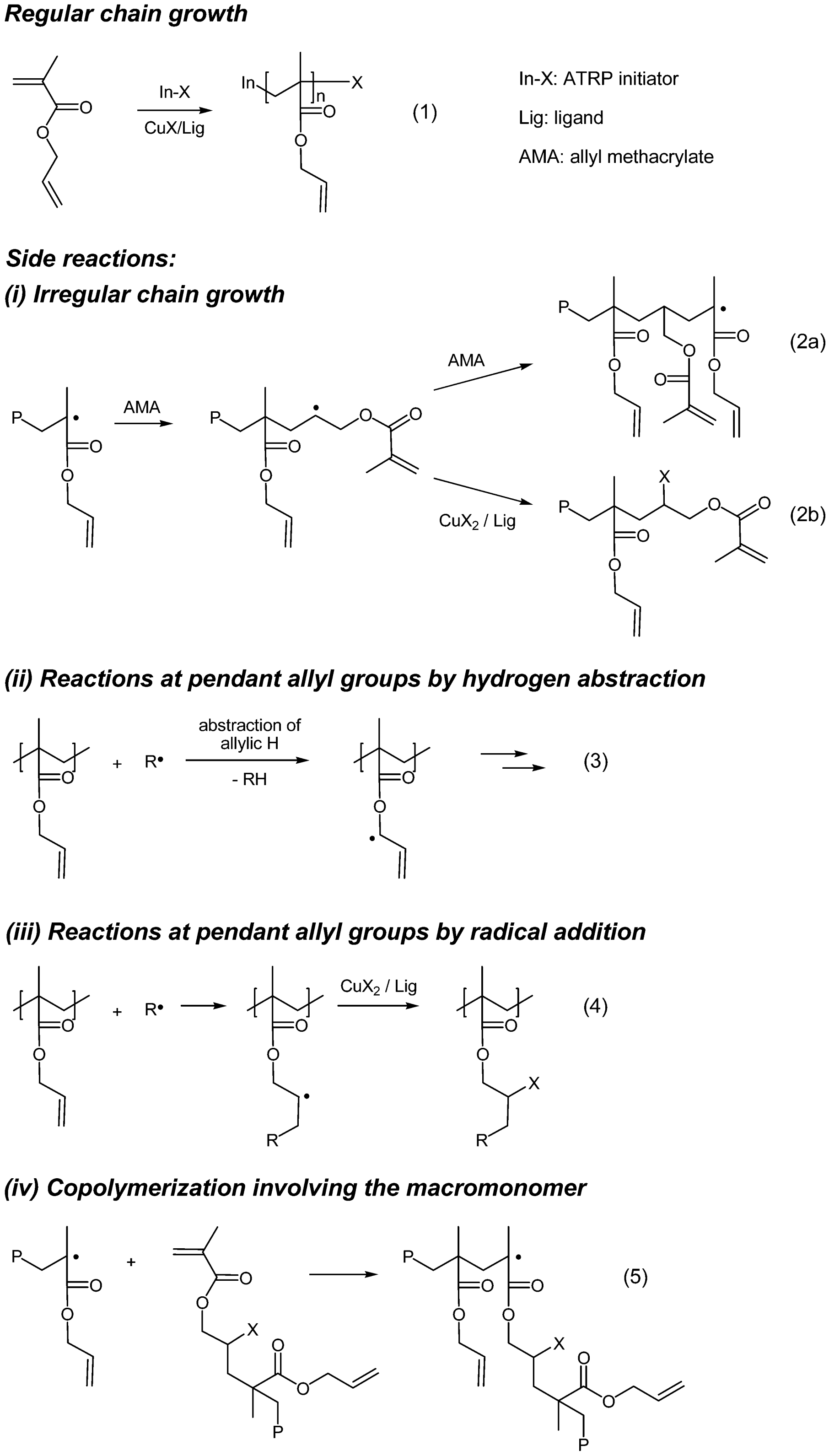
Free radical polymerization of AMA leads to a cross-linked polymer even in the early stages of the reaction.[8,18] Since the existing literature does not contain exact information about molecular weight and molecular weight distribution, we started with preliminary experiments concerning AMA homopolymerization using AIBN as the initiator at 90 °C in *n*-butyl acetate. After 6 min, the conversion was 17% and the molecular weight distribution was multimodal with a polydispersity of 6.7. Gelation was observed after 8 min, which demonstrates that cross-linking had occurred.

In contrast, polymerization of AMA using ATRP offers the possibility to prepare PAMA up to a monomer conversion of ca. 65%. However, beside the regular chain growth reaction involving only the highly reactive methacrylate double bond (Scheme 1, eq 1), side reactions must be considered. The relative importance of the different side reactions is dependent on the conversion; the ratio of methacrylic double bonds to methacryloyl radicals (polymer chain ends) decreases during the reaction. On the other side, the ratio of allylic double bonds (both in monomer and in the repeating units) to methacryloyl radicals remains nearly on a constant level throughout the polymerization. Furthermore, the concentration of allyl groups in the repeating units increases at the expense of monomer allyl groups. On the basis of this background, the following reactions have to be considered: (i) Irregular chain growth reaction (Scheme 1, eq 2) in which the allyl double bond reacts with the active chain end. Lovell and co-workers considered this irregular monomer addition to be the true reason for cross-linking during free radical AMA polymerization (i.e., cross-linking reactions start from the methacrylic pendant groups of AMA units incorporated in a defective way and not from allylic pendant groups; cf. Scheme 1, eq 2a).[4] In the case of ATRP (eq 2b), the irregular addition leads to a highly active radical intermediate, which by reaction with the CuX_2 complex results in a methacrylate macromonomer. The C−X bond formed in this process is not dormant, but is a *dead* species, since this bond is not sufficiently activated under ATRP conditions. This irregular incorporation of the AMA monomer is favored more in the beginning of the reaction due to the relatively high concentration of monomer compared to repeating units; at higher conversion, when the monomer was consumed, side reactions at the allyl groups of the repeating units are favored. (ii) Transfer of hydrogen atoms from the allylic position leads to a resonance stabilized allyl radical with much lower reactivity than methacryloyl radicals and thus low probability to further react with monomers (Scheme 1, eq 3). Although the hydrogen abstraction is theoretically possible for the allyl groups of AMA monomer and repeating units as well, it is significant only for the latter. The reason for that is the very low probability of the hydrogen abstraction at the beginning of the polymerization when methacrylic monomer is sufficiently present and the active radicals add much faster to an acrylate double bond. The probability of H transfer to active polymer radicals increases at high conversion (i.e., monomer concentration becomes low) when the reaction mixture contains mainly AMA repeating units. (iii) Active chain end radicals alternatively may add to an allyl double bond (Scheme 1, eq 4). The resulting radical is not an effective species for reinitiation; since the activation/deactivation equilibrium of ATRP is very fast (necessarily faster than the chain propagation step), the reaction of the radical with the CuX_2 complex (in this case, resulting in an irreversible termination) is much faster than the addition of a monomer unit. The deactivation by the CuX_2 complex results in a C−X bond inactive for ATRP. This latter reaction is very similar to the irregular chain growth reaction (eq 2), however, with a higher probability at high monomer conversion, which is explained by the following: The ratio of allyl groups *at the monomer* to methacryloyl radicals (active chain ends) decreases during the reaction. Simultaneously, the ratio of allyl groups *in the repeating units* to methacryloyl radicals increases with conversion. This circumstance governs the probability of the reactions in eq 2 compared to eq 4. (iv) Finally, the methacrylate macromonomer formed in eq 2 is involved in the AMA polymerization process leading to branched polymers (Scheme 1, eq 5).

As anticipated, homopolymerization of AMA using ATRP proceeds in a well-controlled fashion. *p*-Fluorophenylsulfonyl chloride (FPSC) was used as the initiator since arenesulfonyl halides belong to a universal class of effective initiators for ATRP as pointed out by Percec and co-workers.[19−22] Under conditions commonly applied for the polymerization of methyl methacrylate (CuCl/PMDETA, BuAc as a solvent), conversions up to 65% were obtained without cross-linking, depending on the monomer/initiator ratio and thus on the chain length.

Figure 1a illustrates the dependence of conversion on time which is different from the observation made for free radical polymerization which at a conversion below 20% leads to gelation. The variation of the ratio $[M]_0/[I]_0$ results in two observations: (i) Cross-linking is only observed for $[M]_0/[I]_0$ ratios ≥ 50 (cf. Figure 1a). In the

Scheme 1. Proposed Atom Transfer Radical Polymerization Process under Participation of Allyl Groups



case of $[M]_0/[I]_0 \le 25$, AMA polymerization does not result in a cross-linked product within the time window monitored, but conversion is stopped at a certain level. The maximum conversion is higher the lower the ratio $[M]_0/[I]_0$ is. (ii) The variation of $[M]_0/[I]_0$ influences the slope in the first-order plot (Figure 1b); high concentration of initiator leads to a higher apparent rate constant than low initiator concentration. Deviation from linear relationship at later reaction stages is attributed to termination processes. The dependence of M_n on conversion (cf. Figure 1c) is linear only at low conversion; the slope increases for increasing ratio $[M]_0/[I]_0$ as expected. At higher conversion, however, M_n increases faster than expected, depending on $[M]_0/[I]_0$. At lower ratio $[M]_0/[I]_0$ (and thus at lower degree of polymerization at a given conversion) the deviation from linearity starts at higher monomer conversion: for $[M]_0/[I]_0 = 12.5$, a linear relationship between molecular weight and con-

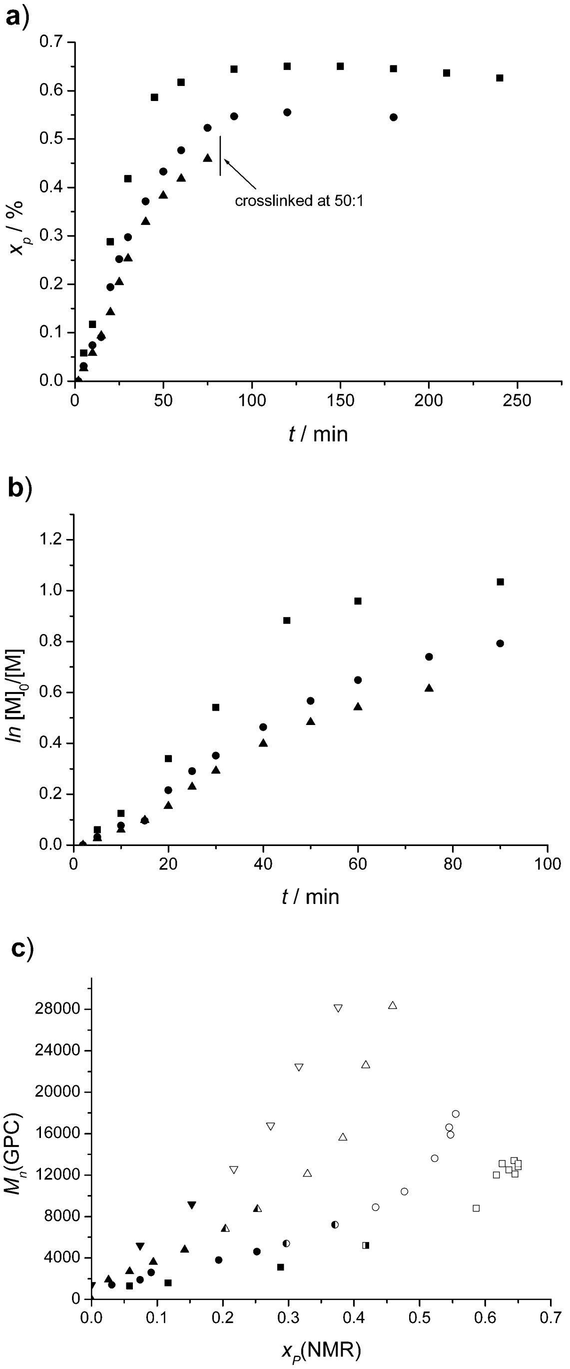


Figure 1. Polymerization of allyl methacrylate using different [M]$_0$/[I]$_0$ ratios (conditions: *p*-fluorophenylsulfonyl chloride/CuCl/pentamethyldiethylenetriamine = 1:1:1.2, T = 110 °C, solvent: *n*-butyl acetate; (■) [M]$_0$/[I]$_0$ = 12.5:1, (●) [M]$_0$/[I]$_0$ = 25:1, (▲) [M]$_0$/[I]$_0$ = 50:1, (▼) [M]$_0$/[I]$_0$ = 100:1): (a) conversion as a function of time; (b) first-order plot; (c) molecular weight as a function of conversion (closed symbols: monomodal symmetric molecular weight distribution; half-opened symbols: asymmetric molecular weight distribution; opened symbols: bi/multimodal molecular weight distribution).

version is observed up to ca. 45%; in contrast to this, a linear dependence for [M]$_0$/[I]$_0$ = 100 was only found below 15%.

Figure 2 illustrates the shape of the GPC curves at different conversions for [M]$_0$/[I]$_0$ = 100:1. At early reaction stage (low conversion), monomodal curves are observed (curve A). At later stages, eluograms become multimodal accompanied by increasing polydispersities (Figure 2, curves B and C). Moreover, the shape of the GPC curves as a function of conversion showed a strong dependence on monomer/initiator ratio. For [M]$_0$/[I]$_0$ = 100 and 50, monomodal molecular weight distributions were obtained only for conversions below 15%. In the contrast, for [M]$_0$/[I]$_0$ = 25 and 12.5, monomodality was observed up to conversions of 30% or more than 45%, respectively.

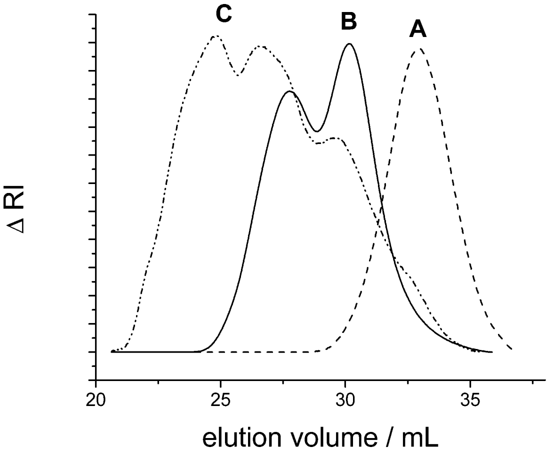


Figure 2. GPC eluograms of allyl methacrylate homopolymerization, [M]$_0$/[I]$_0$ = 100:1, T = 110 °C, *p*-fluorophenylsulfonyl chloride/CuCl/pentamethyldiethylenetriamine, solvent: *n*-butyl acetate; (A) conversion x_p = 0.07; (B) x_p = 0.27; (C) x_p = 0.38.

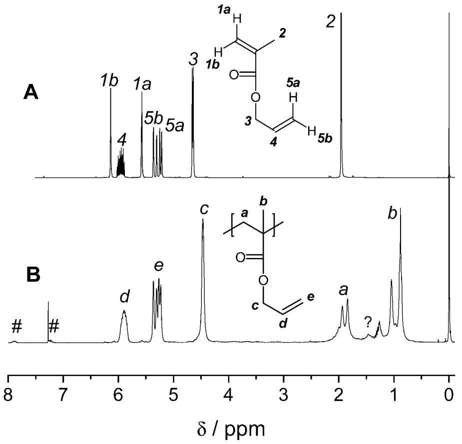


Figure 3. ^{1}H NMR spectra (CDCl$_3$) of (A) allyl methacrylate monomer and (B) poly(allyl methacrylate) (#: end group of initiator *p*-fluorophenylsulfonyl chloride).

The AMA homopolymer was obtained as a solid by precipitation in pentane. The ^{1}H NMR spectra of AMA monomer and polymer are presented in Figure 3 and reveal the presence of allyl double bonds in the polymer (for a more detailed discussion, see below). However, after standing in air without a stabilizer for a day, the polymer becomes partially insoluble due to cross-linking induced by oxygen. This result corresponds to experiments performed by D'Alelio and Hoffend,[11] who observed the same phenomenon on PAMA prepared following the anionic route.

From these experimental data the following conclusions are drawn:

1. The dependence of M_n on conversion indicates a time-dependent relevance of the reaction steps presented in Scheme 1: During early stages, when molecular weight distributions are monomodal (Figure 2, curve A) and M_n increases linearly with conversion (Figure 1c), the predominant process is the regular

chain growth reaction (eq 1). Radical additions to pendant allyl groups (eq 4) are excluded. From a statistical point of view, the probability of irregular chain growth (eq 2) should be higher than in later stages as a consequence of high monomer concentration at this time. If macromonomers are formed during early stages, their GPC signal cannot be distinguished from the signal of other polymer chains due to similar molecular weights. Moreover, these macromonomers do not participate in the polymerization for statistical reasons because their concentration is much lower than that of AMA. Allyl hydrogen abstraction (eq 3) which would lead to a chain termination cannot be of significance during early stages because first-order plots remain linear at low conversion.

2. At higher conversion, the dependence of M_n on conversion is no longer linear (higher M_n values than expected are observed) which coincides with the observation that molecular weight distributions become multimodal. Consequently, processes that have not been of significance in earlier stages now play a role. With respect to Scheme 1, both radical addition to pendant allyl groups (eq 4) and the participation of macromonomers as comonomers (eq 5) are an explanation for this observation. Distinction of these two processes via conventional analytical methods is not feasible.

3. Figure 1a reveals that for those cases lacking gelation the maximum conversion obtainable is limited, depending on the $[M]_0/[I]_0$ ratio. The conversions obtained are significantly below 100%. Therefore, we assume that termination processes via allyl hydrogen abstraction (Scheme 1, eq 3) now gain importance.

4. Comparing free and controlled radical polymerization of AMA and the occurrence of cross-linking, two important differences can be pointed out: (i) The probability of a radical attack at a pendant allyl group is much lower in ATRP than in free radical polymerization since the concentration of radicals is several orders of magnitude lower. (ii) The attack of an active chain at a pendant double bond generates a reactive radical that in free radical polymerization bears the potential of cross-linking reactions upon reaction with a second allyl group. In ATRP, the reactive species is transferred into a dead species by reaction with the Cu(II) complex (Scheme 1, eq 4). Hence, cross-linking is initially suppressed, and the reaction is stopped at the stage of branching, forming a high molecular weight polymer with high polydispersity. Interestingly, already in 1968 Higgins and Weale pointed out for the free radical AMA polymerization that "reactions in which allyl-radical side chains are terminated without crosslinking" ensure the production of soluble polymers.[1] Note that a small amount of Cu(II) species is consumed in this irreversible termination step. However, the persistent radical effect (PRE) ensures the regeneration of the Cu(II) complex.[23] From the statistical point of view, the probability of an attack at pendant double bonds increases at higher conversions since the concentration of monomer decreases and the concentration of pendant allyl groups increases during polymerization. Nevertheless, the M_n vs conversion diagrams for different $[M]_0/[I]_0$ ratios (Figure 1c) prove conversion not to be the only factor playing a role within this context.

5. After an initial phase of a linear M_n vs conversion dependence, the slope increases over-proportionally. It is evident that the deviation from a linear plot and asymmetric/multimodal molecular weight distributions show a clear trend regarding the $[M]_0/[I]_0$ ratio: Nonlinear increase of M_n and deviation from monomodal molecular weight distributions are observed at lower conversion if chain lengths are higher. These results correlate with the conversion/time dependence in which gelation was only observed for $[M]_0/[I]_0 \geq 50$ and not for 25 and 12.5. The "measured conversion" in Figure 1a decreases for longer reaction times in the case of $[M]_0/[I]_0 = 25$ and 12.5. This is attributed to the fact that conversions were determined by comparing OCH_2 proton NMR signals of monomer and polymer, and consequently the latter signal decreases if allyl groups are consumed by branching reactions. We thus conclude that the occurrence of cross-linking is *not* primarily a question of the degree of conversion (the concentration of unreacted vinylic double bonds and allylic double bonds at the repeating unit is shifting to the latter with increasing monomer conversion) but of chain length and entanglement processes as already pointed out by Matsumoto.[5] This aspect is also important when comparing controlled and free radical AMA polymerization: A characteristic feature of free radical polymerization is the achievement of high molecular weights even at low conversions. In contrast, in controlled radical polymerization higher molecular weights are only achieved at higher conversion.

Since only a small amount of allyl groups is involved in the branching process, the major part of unsaturated groups remains unreacted within the repeating units of the polymer chain and offers the potential of further reactions (vide infra).

Resins usually have a low degree of cross-linking. To obtain a wide variety of cross-linkable materials, AMA can be copolymerized, e.g., with St and MMA. Within this paper, we present our results of the copolymerization of AMA with St and the subsequent cross-linking of the obtained polymers. Random copolymers of St and AMA were obtained via polymerization in butyl acetate using standard ATRP procedures. Reactivity ratios of two monomers in a copolymerization are usually very similar for free and controlled polymerization. However, as recently pointed out by Haddleton,[24] significant differences of the monomer reactivity ratios can be found between free radical polymerization and ATRP in special cases; these results are attributed to complex formation between monomer and catalyst which is favored in the case of functionalized monomers containing donor atoms such as N or O.

The copolymers of AMA and St prepared were well-defined at moderate conversions (cf. Table 1). In general, they are completely soluble in standard organic solvents for polystyrene (e.g., CH_2Cl_2, $CHCl_3$, THF, DMAc) and were obtained as white powders upon precipitation from a CH_2Cl_2 solution into methanol.

We started polymerization studies at 110 °C using PMDETA as complex ligand as it was also applied for AMA homopolymerization. The ratio of monomer units in the copolymer was determined by ^{1}H NMR spectroscopy (comparison of $-CH{=}CH_2$ and phenyl group signals at 4.7−6.0 and 6.2−7.5 ppm, respectively) and corresponds to the ratio of monomers in the feed, as observed in all the following experiments. Already after 5 h (Table 1, entries 1 and 2), the GPC elution curves obtained showed a high molecular weight shoulder. When reaction time was raised for $[St]_0/[AMA]_0 = 80:20$, a multimodal molecular weight distribution with very high polydispersity ($M_w/M_n > 22$) was obtained

Table 1. Random Copolymerization of Styrene (St) and Allyl Methacrylate (AMA) in *n*-Butyl Acetate under Varying Reaction Conditions

no.	ligand	temp (°C)	*t* (h)	$[M]_0/[I]_0$	St/AMA in feed (mol/mol)	St/AMA repeat. units in polymer[a] (mol/mol)	M_n GPC[b]	M_w/M_n	GPC curve shape[c]	conv (grav)
1	PMDETA	110	5	50	90:10	90:10	7300	1.21	sh	0.66
2	PMDETA	110	5	50	80:20	80:20	8600	1.62	sh	0.69
3	PMDETA	110	10	50	80:20	82:18	19100	22.44	mu	n.d.
4	PMDETA	110	20	50	90:10	80:20	18200	10.10	mu	0.84
5	PMDETA	110	20	50	80:20	–[d]	–	–	–	–
6	PMDETA	90	5	50	80:20	79:21	4200	1.15	mo	0.34
7	PMDETA	90	10	50	80:20	78:22	6100	1.19	as	0.42
8	Bpy	130	5	50	95:5	96:4	5000	1.18	mo	0.61
9	Bpy	130	5	50	90:10	89:11	5400	1.30	mo	0.61
10	Bpy	130	5	50	85:15	83:17	3300	1.15	mo	n.d.
11	Bpy	130	5	50	80:20	78:22	4700	1.28	mo	n.d.
12	Bpy	130	5	100	80:20	77:23	5300	1.32	mo	n.d.
13	Bpy	130	5	25	80:20	81:19	3700	1.50	as	0.64
14	Bpy	130	20	50	90:10	90:10	5100	1.27	mo	n.d.
15	Bpy	130	20	50	80:20	80:20	4900	1.50	mo	n.d.

[a] Determined by comparison of the integrals of $-CH{=}CH_2$ (4.7–6.0 ppm) and phenyl (6.2–7.5 ppm) resonances in ^1H NMR spectra. [b] M_n was determined using polystyrene calibration; results are not absolute values, but "polystyrene equivalents". [c] Explanation: mo = monomodal, symmetric; as = monomodal, asymmetric; sh = shoulder; mu = multimodal. [d] Cross-linked.

after 10 h (entry 3) whereas after 20 h under the same conditions gelation was observed (entry 5). However, if the AMA content of the feed was lowered from 20 to 10 mol %, a soluble product exhibiting high polydispersity was obtained after 20 h (entry 4). Finally, polymerization temperature was decreased to 90 °C for the application of PMDETA (entries 6 and 7). In contrast to polymerizations carried out at 110 °C, molecular weight distributions were monomodal for $[St]_0/[AMA]_0 = 80{:}20$ after 5 h and even after 10 h (though slightly asymmetric in the latter case). Conversions and polydispersities were lower than in the corresponding polymerizations at 110 °C.

Summarizing these results, the shoulders observed in molecular weight distribution for reaction times of 5 h (entries 1 and 2) represent an early stage of branching reactions which become more obvious at longer reaction times (entries 3 and 4) and finally lead to cross-linking (entry 5). To achieve an increased control by suppression of branching reactions, our strategy was the application of a less reactive ligand in the ATRP catalyst. Lower reactivity might be a promising approach to higher selectivity (i.e., preferential reaction of the active radical with the methacrylic compared to the allylic double bond).

Since Bpy is known to form less reactive ATRP systems,[25] we carried out polymerization studies with the Bpy ligand at 130 °C; these conditions are typical for the atom transfer radical polymerization of styrene. In a first series of experiments (Table 1, entries 8–11) polymerization was carried out at $[M]_0/[I]_0 = 50$ for 5 h using different ratios of monomers in the feed. The four polymers obtained show a monomodal and symmetrical molecular weight distribution; again, the ratio of repeating units corresponds to the ratio in the monomer feed. In a second series of experiments (entries 11–13), the ratio $[M]_0/[I]_0$ was varied. Molecular weights obtained show the expected trend (higher M_n at higher ratio $[M]_0/[I]_0$) although not the expected relation. A possible explanation is a higher contribution of termination via abstraction of an allylic H (cf. Scheme 1, eq 3) which should be favored if the ratio of allyl groups to radicals is high as in the case of large $[M]_0/[I]_0$ values (beside the fact that M_n was determined by GPC using polystyrene standards).

Molecular weight distributions obtained are monomodal as well. Even if reaction times were prolonged to 20 h (entries 14 and 15), monomodal GPC eluograms were obtained; however, despite the longer reaction times, the M_n values do not increase.

Thus, we conclude that in St/AMA copolymerization reactivity of ATRP catalysts is indeed opposed by selectivity: Bpy which forms copper complexes with relatively low reactivity is favorable for the preferential polymerization reaction via the highly reactive methacrylic double bond whereas the radical addition at the allylic double bond—either by irregular chain growth (Scheme 1, eq 2) leading to the formation of macromonomers or by the attack of pendant allyl groups (eq 4)—is only of minor importance. Therefore, the formation of branched or (finally) cross-linked products is suppressed even at higher conversion. In the case of the highly reactive PMDETA ligand, the reactivity of the radical chain end is enhanced, and thus the selectivity toward the methacrylic double bond is less pronounced. Branching and finally cross-linking are even more favored if the AMA content is increased (cf. Table 1, entries 4 vs 5). For the application of PMDETA, a decrease in reaction temperature from 110 to 90 °C leads to higher selectivity and better control at the expense of product yield.

Product Analysis. ^1H NMR spectroscopy clearly reveals the presence of olefinic groups in the copolymer (cf. Figure 4A). All signals are very broad, especially the OCH_2 signal which covers a shift range of more than 1 ppm (peak c in Figure 4). In addition to atacticity, the broadness of all NMR peaks is attributed to the monomer sequence in the random copolymers and corresponds to results reported for P(St-*co*-MMA) in which the signals of the OCH_3 groups cover a range of ca. 2 ppm due to the different chemical shifts of St/MMA triads.[26] Atacticity and sequence distributions represent a clear contrast to results found for the AMA homopolymer (cf. Figure 3, spectrum B): Lines are relatively sharp, and the resonance lines of the methyl groups are split up into three distinct peaks—corresponding to mm, rr, and mr triads—the integral ratios of which imply a high degree of syndiotacticity.

Time-dependent monitoring of the NMR spectra leads to the observation that, with increasing conversion in St/AMA copolymerization, the integral ratio of the olefinic groups compared to the aromatic protons of the St repeating units decreases. This has two reasons:

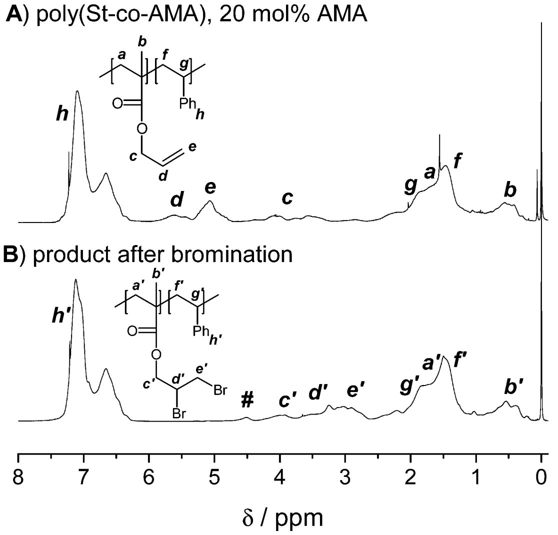


Figure 4. ^{1}H NMR spectra (CDCl$_3$) of (A) poly(styrene-*co*-allyl methacrylate) containing 20 mol % allyl methacrylate repeating units and (B) of the polymer obtained after bromination of A (#: CHBr end group signal).

(i) the preferential incorporation of the AMA monomer in the *early* stages of the polymerization (which was also demonstrated by kinetic measurements, vide infra); (ii) a higher probability of a reaction at the pendant olefinic group (i.e., branching) with increasing conversion (i.e., olefinic groups vanish and the NMR signals of saturated groups formed coincide with the backbone signal).

Moreover, kinetic measurements were carried out for the copolymerization of St and AMA as well. Because of the complex nature of the ^{1}H NMR spectrum of P(St-*co*-AMA) and its poorly resolved signals, the determination of conversion is not possible via NMR. For this reason, conversions were determined by means of GC using the solvent (BuAc) as an internal standard (cf. Figure 5a). A linear first-order behavior is observed indicating a controlled polymerization reaction, depending on the catalyst system (Figure 5b); e.g., for the Cu/Bpy system, linear behavior is observed up to ca. 70% overall conversion. For the Cu/PMDETA system, deviations occur at lower conversions. From the conversion−time plot (Figure 5a) and the first-order plot (Figure 5b) it is seen that AMA is incorporated faster than St, leading to a gradient structure of the copolymer. For example, for the copolymerization of a 80/20 mixture of St/AMA using Bpy at 130 °C, the ratio of St vs AMA repeating units is 73/27 at 15% total monomer conversion and increased over 75/25 at 48% up to 77/23 at 80% conversion (cf. Figure 5).

In the kinetic studies, polymerizations were monitored in a time window up to the point when monomer conversion showed no further increase (Figure 5a). Within this time window, molecular weights increase nearly linearly with conversion; at lower conversions, M_n values measured are slightly above the values expected for a linear growth which is explained by the preferential incorporation of AMA during early stages and the higher mass of the AMA repeating unit compared to the styrene repeating unit (126 vs 104 g/mol). Within the observed time window GPC curves remained monomodal with low polydispersities indicating the controlled/"living" nature of the polymerization process. However, some of the polymerization results presented in Table 1 clearly exceed this time window and show multimodal molecular weight distributions. As in the case of AMA homopolymerization, these processes are either the results of an attack of growing polymer chain ends at a pendant olefinic group followed by an irreversible termination step (cf. Scheme 1) or the participation of macromonomers as a third component beside St and AMA. Monitoring of these new groups formed after irreversible termination by ^{1}H NMR spectroscopy is not feasible since the expected concentration

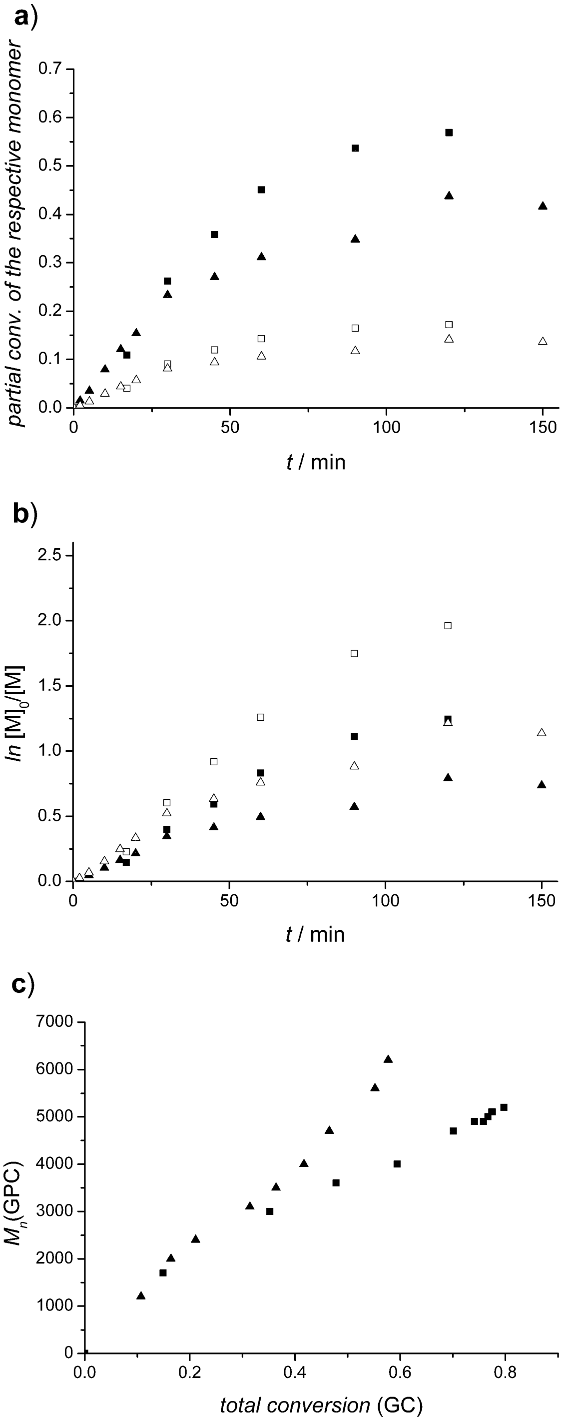


Figure 5. Copolymerization of styrene (St) and allyl methacrylate (AMA) using different reaction conditions (initiator: (1-bromoethyl)benzene; solvent: *n*-butyl acetate; $[St]_0/[AMA]_0/[I]_0 = 40:10:1$; (■) 2,2′-bipyridine, 130 °C; (▲) pentamethyldiethylenetriamine, 110 °C). Closed symbols represent experimental values for St and opened symbols for AMA. (a) Partial conversions as a function of time; (b) first-order plot; (c) molecular weight as a function of conversion; GPC curves remain monomodal for all experiments displayed.

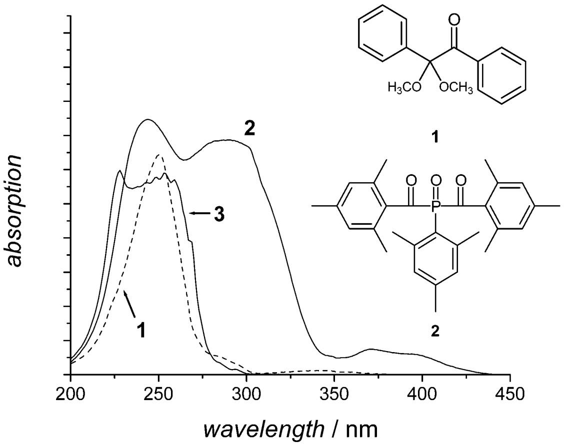


Figure 6. UV spectra of the photoinitiators 2,2-dimethoxy-2-phenylacetophenone (**1**) and bis(2,4,6-trimethylbenzoyl)-phenylphosphine oxide (Irgacure 819, **2**) and UV spectrum of poly(styrene-*co*-allyl methacrylate) with an 80/20 ratio of styrene/allyl methacrylate repeating units (**3**). All spectra recorded in THF at room temperature.

of these groups is very small and the expected signals coincide with the signals of the repeating unit.

Because of the lower concentration of cross-linkable groups compared to AMA homopolymerization (cf. Figure 1a), in AMA/St copolymerization higher monomer conversions (depending on the amount of AMA in the copolymer) are achieved (cf. Figure 5a).

Reaction of the Pendant Double Bonds. *Bromination.* To ensure NMR group assignment and allyl group reactivity of poly(styrene-*co*-allyl methacrylate), bromination was chosen as a typical reaction. Bromination of the copolymer was easily achieved by dissolution in dichloromethane and addition of bromine at 0 °C. ^{1}H NMR spectroscopy revealed that double bonds were completely consumed (cf. Figure 4B).

Cross-Linking Reactions. Cross-linking of the copolymers was carried out by both thermal and photochemical initiation. First investigations using 2,2-dimethoxy-2-phenylacetophenone (cf. Figure 6, structure **1**) as a typical photoinitiator did not lead to the formation of insoluble products. Considering the UV spectra of P(St-*co*-AMA) and of 2,2-dimethoxy-2-phenylacetophenone (cf. Figure 6, curves **1** and **3**), the reason can be found in the UV absorption of the styrene repeating units. Consequently, we decided to employ special initiators of the Ciba Irgacure family designed for photoinitiation in the presence of UV stabilizers (cf. Figure 6, structure/curve **2**).

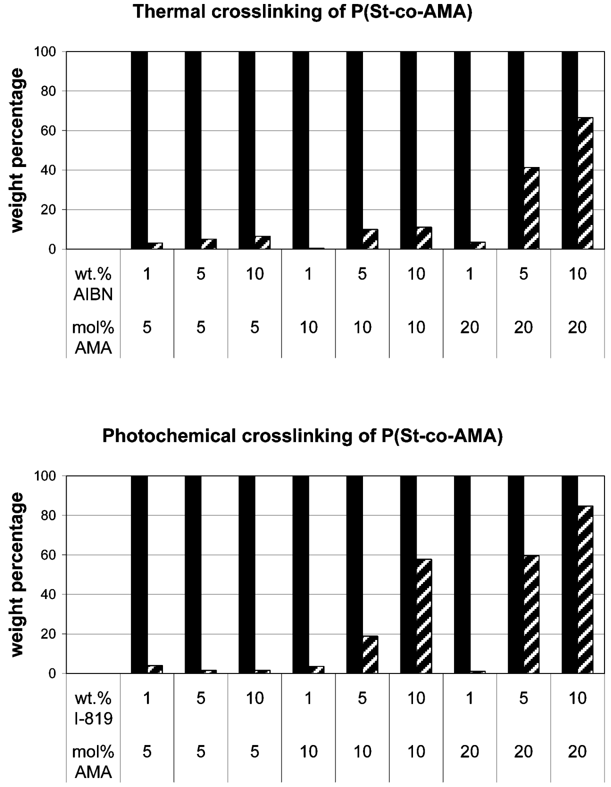


Figure 7. Results of the cross-linking reactions of poly(styrene-*co*-allyl methacrylate): (a) thermal cross-linking using 2,2′-azobis(2-methylpropionitrile) (AIBN) as the initiator, (b) photo-cross-linking using bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (Irgacure 819); plain columns: soluble starting material; hatched columns: insoluble residue.

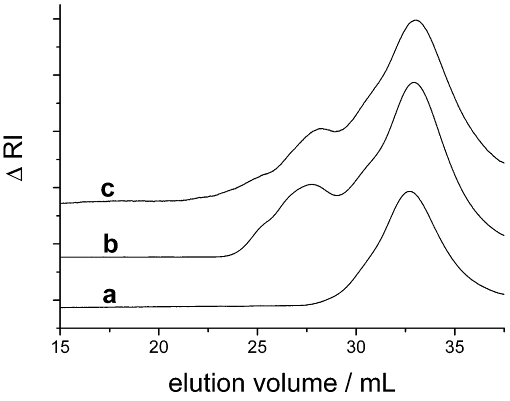


Figure 8. GPC eluograms of (a) poly(styrene-*co*-allyl methacrylate) (10 mol % allyl methacrylate), (b) soluble part of the product obtained after treatment with 10 wt % 2,2′-azobis(2-methylpropionitrile) at 100 °C for 24 h, and (c) soluble part of the product obtained after treatment with 10 wt % bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide (Irgacure 819) under UV irradiation for 3.5 h.

In our studies, both the content of olefinic pendant groups and the concentration of initiators were varied (copolymer: up to 20 mol % of AMA repeating units; intitiator: up to 10 wt %). A polymer film containing the initiator was prepared (thickness < 1 mm) and then irradiated with UV light or heated. Depending on the initiator and double bond concentration, the products obtained after UV irradition for 3.5 h became partially insoluble in CH_2Cl_2, $CHCl_3$, THF, or DMAc. This is attributed to network formation. Similar results were obtained after application of AIBN followed by heating at 100 °C for 24 h. Since this period is significantly above the half-life of AIBN at this temperature, a complete decay of the initiator is assured; however, thermal initiators with longer half-lifes could be of advantage for a higher degree of cross-linking. To estimate the extent of cross-linking, the weight of the insoluble product was compared with the initial mass. The results presented in Figure 7 show that under the conditions chosen an initiator content of at least 5 wt % and a double bond content of 20 mol % (for thermal cross-linking) or 10 mol % (for photo-cross-linking) are a prerequisite for a high degree of cross-linking. GPC analyses of the soluble part of the samples (cf. Figure 8) show that the major part of these samples now contains higher molecular weight products which are considered as the preliminary stage of a cross-linked network. The comparison with the GPC curves obtained during AMA homopolymerization (Figure 2) reveals that, in the latter case, a product of much higher molecular weight is formed. Thus, it is concluded that in the ATRP of AMA cross-linking is suppressed, and consequently, a branched high molecular weight product is obtained before cross-linking finally starts. In contrast to that, during the reaction of P(St-*co*-AMA) with thermal initiators or photoinitiators, cross-linked products are formed right from the beginning despite a lower concentration of cross-linkable groups in the polymer. This is explained by the fact that thermal and photochemical cross-linking procedures are *free* radical polymerizations, and thus irreversible termination reactions at the allyl groups—as they occur in ATRP—are insignificant.

Though a contribution of thermal polymerization cannot be completely excluded for the photopolymerization process due to heat evolution by the UV lamp, the results in Figure 7 reveal that the photochemical process obviously is the more effective one. Moreover, it represents a very promising approach since it offers the opportunity of application in lithography.

Conclusion

Allyl methacrylate was homopolymerized and copolymerized with styrene using ATRP. Kinetic studies reveal that polymerizations proceed in a controlled fashion. Cross-linking reactions were prevented up to high conversions, and polymerization yielded soluble products. By adjusting the degree of polymerization in AMA homopolymerization via the monomer/initiator ratio, it was demonstrated that the crucial parameter for the occurrence of cross-linking reactions is the degree of polymerization. Copolymerization of AMA with St resulted in an even better control of the reaction than for AMA homopolymerization. AMA/St copolymers were both brominated and cross-linked. The latter reaction was achieved both thermally and photochemically and underlines the potential of the reported copolymers for applications such as coatings or the formation of (semi)-interpenetrating polymer networks.

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