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Structural control in radical polymerization with 1,1 diphenylethylene: 2. Behavior of MMA–DPE copolymer in radical polymerization

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Abstract

Copolymers of 1,1-diphenylethylene (DPE) behave in a very special way in radical polymerization. Particularly, the behavior of MMA–DPE copolymers in radical polymerization is investigated. The results reveal that the semiquinoid structure of the precursor polymer identified in a previous contribution is activated by the attack of free radicals and thus, in a second stage polymerization with a second monomer, block copolymers are formed. The block copolymer yield depends strongly on the ratio between the amount of DPE-containing precursor polymer and the initiator and monomer concentration used in the second stage. The mechanism proposed is able to explain at least qualitatively all experimental results including the restriction of this mode of control of radical polymerization to the formation of diblock copolymers only.

Keywords: Radical polymerization; Structure control; 1,1-Diphenylethylene

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1. Introduction

The term ‘structural control’ in radical polymerization is mostly associated to the well known techniques of controlled free radical polymerization, like nitroxide mediated polymerization [1,2] metal catalyzed atom-transfer radical polymerization (ATRP) [3,4], and reversible addition-fragmentation chain transfer (RAFT) processes [5–8]. In fact, these processes allow the control of molecular weight or the preparation of polymers with defined structure (various kinds of block copolymers or functional polymers). A great deal has been done during the last decade to explore controlled free radical polymerization processes including the transference of the polymerizations from organic solution into aqueous heterophase polymerization systems. Summaries of this development can be found in [9,10] and proof the achievements of the research as well as point out the pros and cons of each of these techniques. In practical applications, it is however not the control of molecular weight or obtaining a low polydispersity which are intended alone but improved material properties. Furthermore, - all the above cited techniques to control radical polymerization possess some other drawbacks such as in the case of nitroxide mediated polymerization in many cases the utilization of high temperature, or difficulties to remove the metal catalyst in ATRP at the end of the polymerization, and the pollution of the final polymer with halogen and sulfur in the case of ATRP and RAFT techniques, respectively. These are some of the reasons for ongoing searches for efficient and reliable techniques to control polymeric structure in radical polymerizations.

Recently it was found that the use of 1,1-diphenylethylene (DPE) in conventional free radical polymerization allows a high degree of structural control [11]. The principle of this new method consists of a two-step polymerization. In the first step a DPE-containing precursor polymer is prepared, which in a second polymerization leads to the formation of block copolymers. The two steps can be carried out either sequentially and spatially separated or conducted like a one pot synthesis with consecutive addition of monomers. In contrast with the above methods, the DPE-based technique can be applied for all types of acrylate, methacrylate, vinyl and styrene monomers. Moreover, it can

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be applied in bulk, solution as well as heterophase polymerizations [12].

Furthermore, the reaction rates during the second step polymerization are higher compared with the other techniques of controlled radical polymerization. In fact, the rate of polymerization is in the same order of magnitude as for conventional free radical polymerization. For example, a methyl methacrylate precursor polymer can be used to prepare poly (methyl methacrylate)–polystyrene block copolymers in bulk polymerization [13]. Other examples describe the application of hydrophilic precursor polymers in aqueous heterophase polymerization leading to surfactant free high solids block copolymer dispersions with improved properties for various coating applications [14].

However the mechanism of this special kind of control in radical polymerizations is still unclear although some ideas have already been proposed [12,13]. The first proposal is a mechanism similar to the RAFT process where the thermal decomposition of the bond between two DPE units in the precursor polymer is assumed to generate macroradicals, which initiate chain growth and block copolymer formation [12]. In a subsequent publication, the authors suppose the existence of more than one mechanism, depending on the monomer type [13]. But all these ideas suffer from the lack of supporting experimental evidence.

Experimental results with respect to the role of DPE in radical polymerization as well as a proposal of the structure of the copolymers formed have been reported already in a preceding publication [15]. It was experimentally verified that DPE is incorporated into the copolymers, which will be denoted subsequently synonymously also as precursor polymers, as semiquinoid structural unit (so-called α,p-dimers, cf. Formula 1). This structure is formed as the result of combination termination between two DPE-ended growing radicals in accordance with the termination reaction of various kinds of low molecular weight benzyl radicals (cf. [15] and references therein). The aim of this contribution is to report analytical results on the behavior of methyl methacrylate precursor polymers during the second stage polymerization and to shed some light on the mechanism of block copolymer formation. In addition, results of model experiments concerning the products formed after radical attack on the precursor polymer in the absence of monomer are communicated. Finally, an example for the formation of block copolymer dispersions via this kind of structure control in radical polymerization is given utilizing a hydrophilic precursor polymer made by copolymerization of methyl methacrylate and acrylic acid in the presence of DPE.

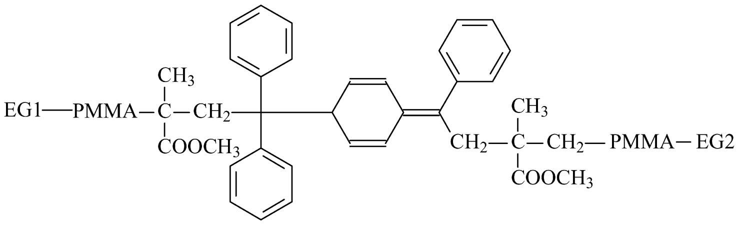
2. Experimental and analytical section

2.1. PMMA–DPE copolymer synthesis

Methyl methacrylate (MMA, 99% purity, Aldrich) was distilled under reduced pressure before use. 1,1-diphenylethylene (DPE, 99% purity, Acros), sodium dodecylsulfate (SDS extra pure, 99% purity, Roth) and ammonium peroxodisulfate (APS, purity ≥98%, Sigma) were used as received. The water was taken for all experiments from a Seral purification system (PURELAB Plus™) with a conductivity of 0.06 $\mu S\ cm^{-1}$ and was degassed prior to use for the polymerizations. The polymerizations were carried out batchwise in a 2000-ml all-glass reactor with a heating jacket to control the polymerization temperature. The reactor was equipped with stirrer, reflux condenser, nitrogen inlet and outlet, a valve on the bottom to take samples during polymerization and dropping funnel to drop the initiator solution.

530.0 g of degassed water and 3.3 g of SDS were introduced under nitrogen in the polymerization reactor. 285.8 g of distilled MMA, 15.3 g of DPE and 99.9 g of ammonia solution buffer (≥25% in water, p. a. Roth, Germany) were charged under stirring and purged with nitrogen. The mixture was heated to reaction temperature at 70 °C. After at least 30 min the temperature was equilibrated, and the polymerization was started by dropping slowly over a period of time of 10 min 22.6 g of APS dissolved in 52.5 g of water. After 8 h the polymerization was stopped.

The obtained latex was purified by ultrafiltration through a regenerated cellulose membrane with a cut-off of 5000 $g\ mol^{-1}$ (Ultran RC/5, Schleicher & Schuell, Germany). Distilled water was refilled and the ultrafiltration continued until the conductivity of the filtrate was constant. The polymer was isolated by freeze-drying. After freeze-drying, the obtained solid was purified by repeated dissolution and precipitation cycles. After dissolution in THF, the THF solution was poured into an excess of methanol. The polymer was isolated by filtration, washed with methanol, and dried. Thereafter this procedure was



Formula 1. Semiquinoid structure of the MMA–DPE precursor polymer.

repeated with cyclohexane instead of methanol as precipitant. The precursor polymer has a weight average molecular weight (M_w) of 7.900 g mol^{-1}, a number average molecular weight (M_n) of 4.000 g mol^{-1}, and contains two DPE units per molecule as described in Ref. [15] (cf. Formula 1).

2.2. Thermal decomposition experiments of the PMMA–DPE copolymer

For the thermolysis experiments, thiophenol (99% purity, Aldrich) was used as radical scavenger. 0.3 ml of thiophenol and 28 mg of MMA–DPE copolymer were dissolved in 2 ml of tetrahydrofuran-d$_8$ (99.5 at.% D, Aldrich) as solvent. 1.2 ml of this solution were put into NMR tube, purged with argon, sealed, and heated to 60 °C. The reaction between thiophenol and MMA–DPE copolymer was followed on-line by ^{1}H-NMR spectroscopy.

2.3. Second step solution polymerization

The polymerizations were conducted with a rotational thermostat VLM20 (VLM GmbH, Leopoldshöhe, Germany) in glass vials at 80 °C for 38 h. The agitation of the polymerization system is due to an end-over-end rotation of the glass vials. About 10 revolutions per minute provide sufficient mixing. The use of this kind of rotational thermostat allows to carried out simultaneously 24 polymerizations and hence to prove the reproducibility of the experiment. 226 mg MMA–DPE copolymer, 1.5 g distilled MMA, 1.4 mg 2,2′-azobisisobutyronitrile (AIBN) and 7.5 g distilled THF were charged in the polymerization vial and purged with nitrogen. The mixture was heated to reaction temperature at 80 °C and the polymerization was conducted for a certain period of time while samples were taken at different times in order to follow the development of the conversion. The polymer was isolated by precipitation in methanol and washed by redissolution in THF and reprecipitation in methanol. For comparison purposes, polymerizations were carried out in the absence of the DPE containing precursor polymer.

2.4. Model reaction

800 mg MMA–DPE copolymer and 800 mg AIBN were dissolved in 400 g distilled THF. This reaction mixture was purged with argon and then transferred into a 100 ml all-glass reactor, which was then heated and kept at 60 °C.

2.5. (Acrylic acid)-co-(methyl methacrylate)-co-DPE copolymer synthesis

Methyl methacrylate (MMA, 99% purity, Aldrich) and acrylic acid (AA, 99% purity, Aldrich) were distilled under reduced pressure before use. 1,1-diphenylethylene (DPE, 99% purity, Acros) and ammonium peroxodisulfate (APS, purity ≥98%, Sigma) were used as received. The polymerization was carried out batchwise in a 2000-ml all-glass reactor. 525.5 g of degassed water was introduced under nitrogen in the polymerization reactor. 102.0 g of distilled MMA, 183.1 g of distilled AA, 15.3 g of DPE and 99.1 g of ammonia solution buffer (≥25% in water, p.a, Roth) were charged under stirring and purged with nitrogen. The mixture was heated to reaction temperature at 70 °C. After at least 30 min the temperature was equilibrated, and the polymerization was started by dropping slowly over a period of time of 10 min 22.6 g of APS dissolved in 52.5 g of water. After 8 h the polymerization was stopped.

The obtained latex was purified by tangential flow ultrafiltration through a low protein-binding modified poly(ether sulfone) membrane with a cut-off of 5000 g mol^{-1} (Minisette™ OMEGA 5Kd from Pall Gelman Laboratory, Germany). Distilled water was refilled and the ultrafiltration continued as long as the conductivity of the filtrate was constant. The polymer was isolated by freeze-drying.

2.6. Second step heterophase polymerization

The polymerizations were conducted with a rotational thermostat VLM20 (VLM GmbH, Leopoldshöhe, Germany) in glass vials at 80 °C for 8 h. Solutions of surfactant and initiator (4,4′-azobis(4-cyanopentanoic acid))in water were prepared beforehand and then freshly distilled styrene was added. The total reaction volume in each vial was 8.6 ml. Before polymerization the reaction mixtures were purged with argon. At the end of the polymerization, the separation of the polymeric products was carried out as follows. One millilitre of the latex was precipitated in 50 ml of acetone. The precipitate, which was according to FT-IR analysis (Biorad FTS 6000 spectrometer) homo-polystyrene, was separated from the solution. The acetone solution was dried up and the solid was dissolved in water. Only the AA-Monomer-DPE precursor copolymer is soluble in water, whereas the copolymer of the precursor copolymer and styrene was found to be insoluble. The precipitate was separated from the solution, dried in vacuum at 50 °C, and calibrated.

2.7. Size exclusion chromatography (SEC) in THF

SEC was performed using a P1000 pump from the firm Thermo Separation Products (TPS), equipped with a RI-detector (Shodex RI-71) and UV1000 detector ($\lambda = 260$ nm, TPS). SEC was worked at 30 °C with distilled tetrahydrofuran (THF) eluent at a flow rate of 1 ml min^{-1}. A column set was employed consisting of three 5 μm 8 × 300 mm columns filled with a MZ Gel Sdplus spherical polystyrene gel with 10^6, 10^5, 10^3 Å from MZ Analysentechnik. The molecular weights were derived from a calibration curve relative to polystyrene standards (PSS, Mainz, Germany).

2.8. UV–VIS spectroscopy

UV-spectra were recorded with a Uvikon 931 photometer from Kontron Instruments S.P.A, Milan, Italy. All spectra were recorded in acetonitrile solution except STO5 and pure polystyrene where chloroform was used as solvent.

2.9. NMR

^{1}H and ^{13}C-NMR spectra were obtained with a Bruker DPX-400 spectrometer in $CDCl_3$ or THF-d_8 at room temperature. ^{1}H chemical shifts were referenced to TMS via the residual non-deuterated solvent signal (at $\delta = 7.23$ ppm for $CDCl_3$ and at $\delta = 1.72$ and 3.57 ppm for THF-d_8).

3. Results and discussion

The semiquinoid structure of the MMA–DPE precursor polymer as described in Ref. [15] is supposed to be the active part that controls the behavior during the second stage polymerization (cf. Formula 1).

In general there exist two different possibilities to activate the semiquinoid structure that is to initiate the formation of growing radicals. Radical formation might be possible either by thermal decomposition or by activation due to the attack of foreign radicals. In the context this contribution it is necessary to mention that both possibilities are known from investigations of the rearrangement of semibenzenes in organic chemistry [16–18]. There is clear experimental evidence that low molecular weight semibenzenes convert into the corresponding benzene derivatives via a radical path (cf. Chart 1) initiated either thermally or photochemically. The conditions of the rearrangement and the preceding homolytic radical formation depend on the particular groups attached at the semibenzene ring. For instance, the optical active (−)ethyl 4-trichloromethyl-2,4,5,-trimethyl-2,5-cyclo-hexadienyleneacetate is described to react only slowly with thiophenol at 120 °C. The intermolecular radical reaction path is concluded from the corresponding racemic reaction product (ethyl α-(2,4,5-trimethylphenyl)-β,β,β-trichloropropionate) [16]. Another example is the rearrangement of 4-allyl-2,3,4,5,6-pentamethyl1-methylenecyclohexa-2,5-diene into 1-(3-butenyl)-2,3,4,5,6-pentamethylbenzene that was largely completed after one week at room temperature [17]. Also, the α,p-dimer of the benzyl radical converts into the α,α-dimer via a radical mechanism however this rearrangement is much faster [18].

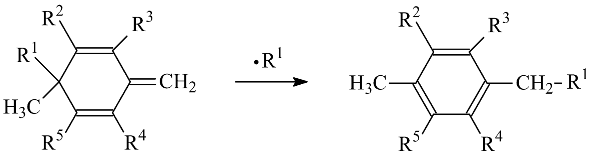


Chart 1. Rearrangement of semibenzenes to benzenes via radical route according to Ref. [16–18].

Moreover, radical formation by thermal decomposition of the precursor polymer might appear reasonable due to the similarity of the DPE-containing precursor with products obtained during radical polymerization initiated with tetraphenyl-substituted ethane compounds [19–23]. But already first screening experiments (heterophase polymerizations of different monomers) in the presence of the hydrophilic precursor polymer (that is the terpolymer made of MMA, acrylic acid and DPE) revealed that this kind of radical formation obviously does not apply as the second stage polymerization was only observed for monomers that are able to thermal self-initiation such as styrene or MMA. In contrast, with vinyl acetate or benzyl methacrylate, both are not able to initiate thermally polymerization, no conversion in the second stage polymerization was observed [24]. The inability of thermal radical formation also of the hydrophobic MMA–DPE precursor polymer was proved by reaction with thiophenol as radical scavenger according to the reaction scheme depicted in Chart 2. If radicals are formed during thermal treatment of the precursor polymer they should attack the SH-group of the thiophenol and ^{1}H-NMR measurements should reveal a decrease in the intensity of S–H proton signal at $\delta = 3.9$ ppm. In accordance with above polymerization results no decrease of the SH proton signal from thiophenol was observed over a period of time of 20 h. These results clearly prove that neither in the hydrophilic nor in the hydrophobic precursor polymer the semiquinoid structure is able to undergo homolytic thermal cleavage.

In order to get a deeper insight in the mechanism of the second stage polymerization MMA was polymerized in THF solution initiated with AIBN in the presence as well absence of the hydrophobic MMA–DPE precursor polymer. Typical results of these investigations are depicted in Fig. 1. These data show that the PMMA–DPE copolymer influences both the polymerization kinetics and the molecular weight. In fact, the presence of the precursor polymer causes a decrease in the polymerization rate (Fig. 1(A)) and in the molecular weight (Fig. 1(B)), compared with a conventional free radical polymerization. The delay in the conversion-time-behavior which is caused by the presence of the precursor polymer is clear to see. The jump in the conversion after about 8 h in the presence of the precursor polymer corresponds almost to the time when thermal MMA polymerization starts to increase remarkably as it was checked by reaction calorimetry (data not shown here). Thus, the jump might be the results of an additional contribution due to thermal MMA polymerization. The molecular weight distribution curves in the case of the conventional MMA solution polymerization show the expected shift towards decreasing molecular weights and practically no change in the shape of the distribution curves with increasing polymerization time. The GPC data for the polymerization in the presence of the precursor polymer

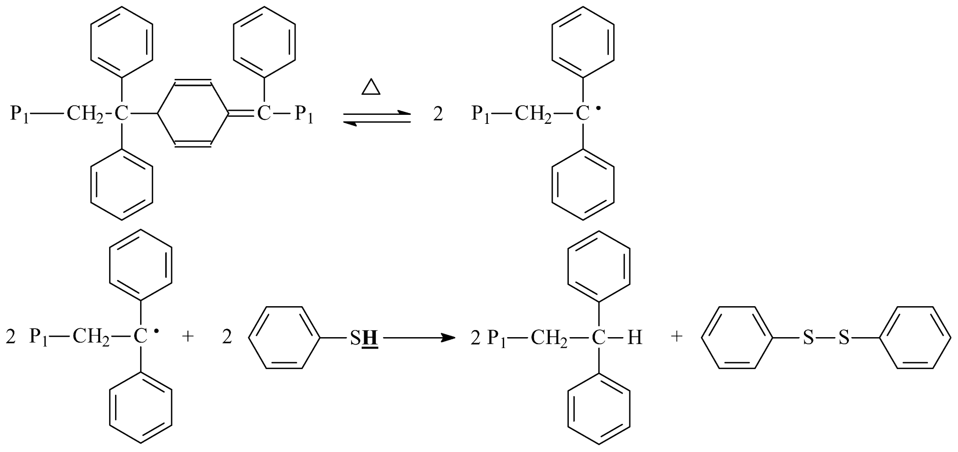


Chart 2. Possible reaction pathway of the thermal decomposition of the precursor polymer in the presence of thiophenol.

show with progressive polymerization a decrease in the intensity of the shoulder in the low molecular weight region that corresponds to the precursor polymer, which means that it is activated and taken up throughout the polymerization process. Moreover, the molecular weights are lower compared to those of the polymerization in the absence of the precursor polymer. Both the lower rates and the lower average molecular weight caused by the presence of the

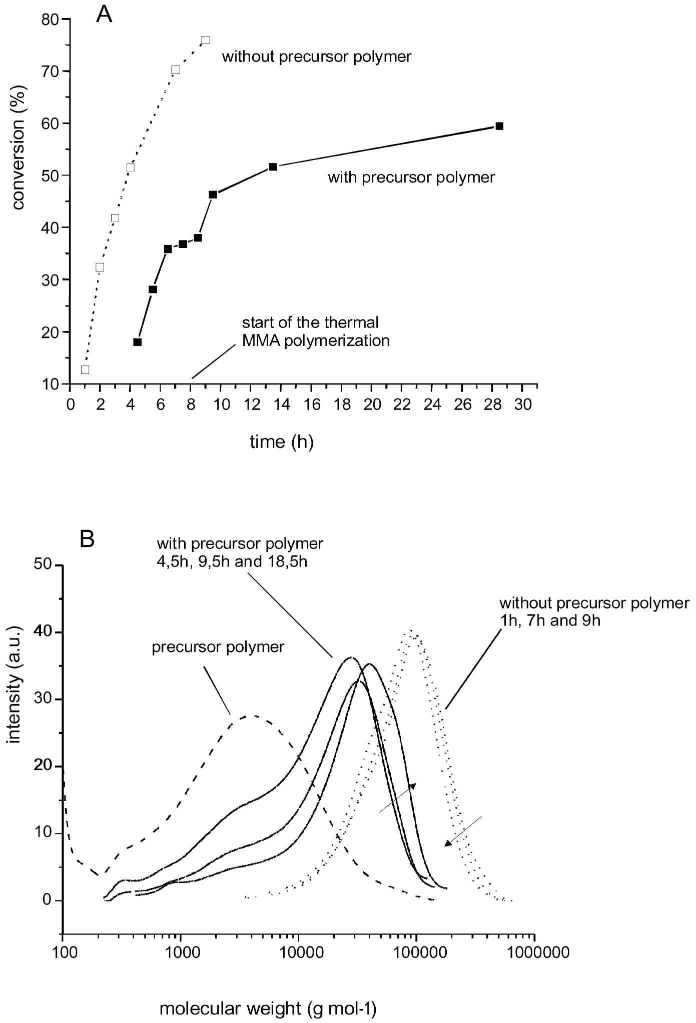


Fig. 1. Influence of the presence of the PMMA–DPE copolymer on the polymerization kinetics (A) and on the molecular weight (B); the arrows indicate the direction of the change of the molecular weight distribution with increasing polymerization time

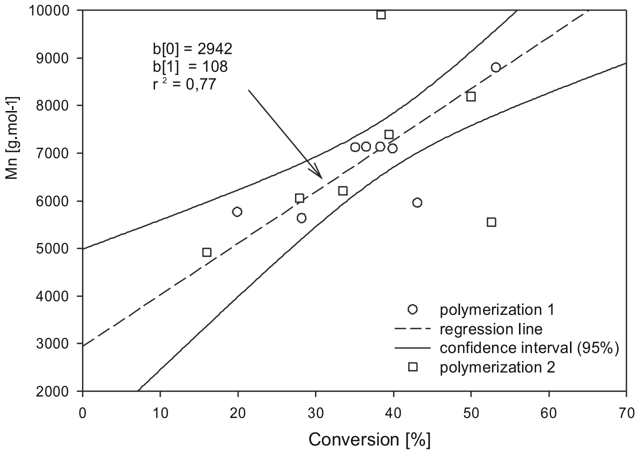


Fig. 2. Molecular weight—conversion plot for free radical polymerization of MMA in the presence of the PMMA–DPE copolymer.

precursor polymer show that it acts comparable with a degradative chain transfer agent [25]. Furthermore and in contrast to a conventional free radical polymerization, the molecular weight distribution is shifted towards higher molecular weights with increasing polymerization time. The increase in the molecular weight is also illustrated by the number average molecular weights put together in Fig. 2. This effect however indicates that the presence of the precursor polymer leads also to a certain control of the radical polymerization process.

The results so far indicate that although the DPE-containing precursor polymers are unable to form radicals by thermal activation alone, they are able to react with radicals during radical polymerization.

In order to get some ideas about the mechanism of this reaction the decomposition of AIBN in the presence of only precursor polymer (in the absence of second stage monomer) was investigated. The SEC-data (Fig. 3(A), refractive index signals) clearly prove that the PMMA–DPE copolymer is not inert against the attack of radicals. With increasing reaction time the high molecular weight part of the molecular weight distribution is shifted towards lower molecular weights (higher elution volumes) and the molecular weight distribution is sharpening during the reaction. Furthermore, a new peak in the molecular weight distribution is observed with increasing reaction time in the low molecular weight region at about 33 ml elution volume whereas the intensity of the AIBN peak decreases. Note, in two sets of comparison experiments it was shown that the molecular weight distribution of both homo PMMA in the presence of AIBN and of the precursor polymer in the absence of AIBN do not change under the particular conditions within the scatter of the experimental error.

The attack of radicals on the DPE-containing precursor polymer changes also the UV-absorption spectra of the latter. Fig. 3(B) reveals that the absorption maximum at

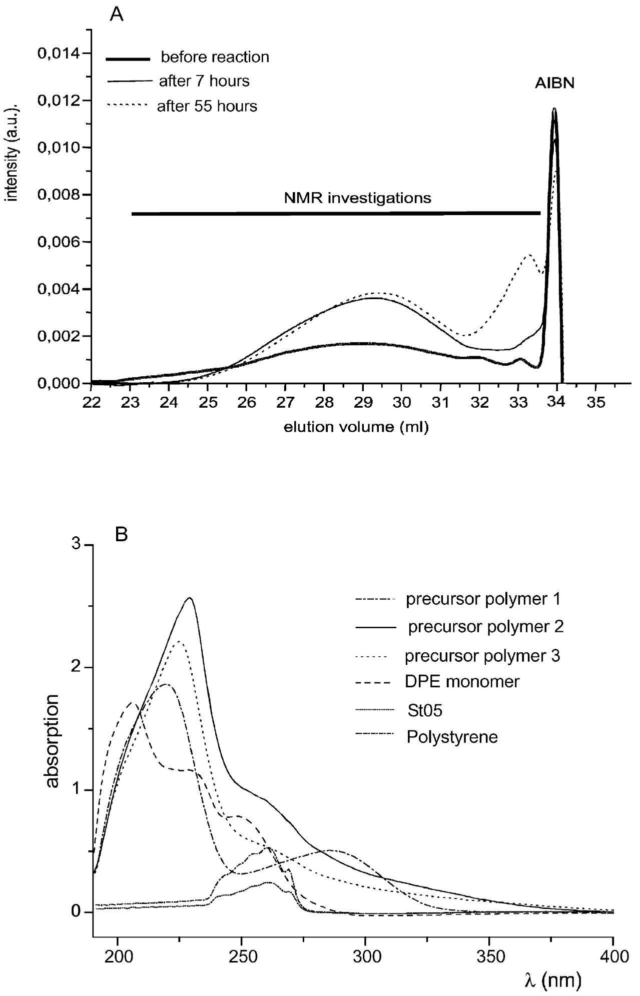


Fig. 3. (A) SEC traces to record the reaction between the precursor polymer and AIBN in THF. (B) UV–Vis absorption spectra of the precursor polymer before (1) and after (2) the model reaction with AIBN, as well as after reaction with bromine (3) in comparison with the absorption spectra for DPE, pure polystyrene, and oligomer of polystyrene with about 5 styrene units, a *t*-butyl start group, one DPE connecting unit, and a propylsulfonate endgroup (STO5, cf. [26]).

about 285 nm of the precursor polymer disappears after the reaction with AIBN. But the reaction products still contain UV-active groups as a new absorption region appears between 250 and 275 nm in form of a shoulder. The whole spectrum of the reaction product resembles that of the product after the reaction of the precursor polymer with bromine (cf. also [15]). The wavelength region of the shoulder in the UV-spectra of both reaction products is almost identical with the absorption of both styrene oligomers with only one DPE unit (sample STO5, cf. [26]) and pure polystyrene initiated with AIBN. But also the spectral range of the bathochromic absorption band of DPE coincides almost with the spectral region of the shoulders in the reaction products. This clearly indicates that during the reaction with isobutyronitrile radicals the extended π-electron system of the semiquinoid structure is destroyed. Together with the decrease in the molecular weight during

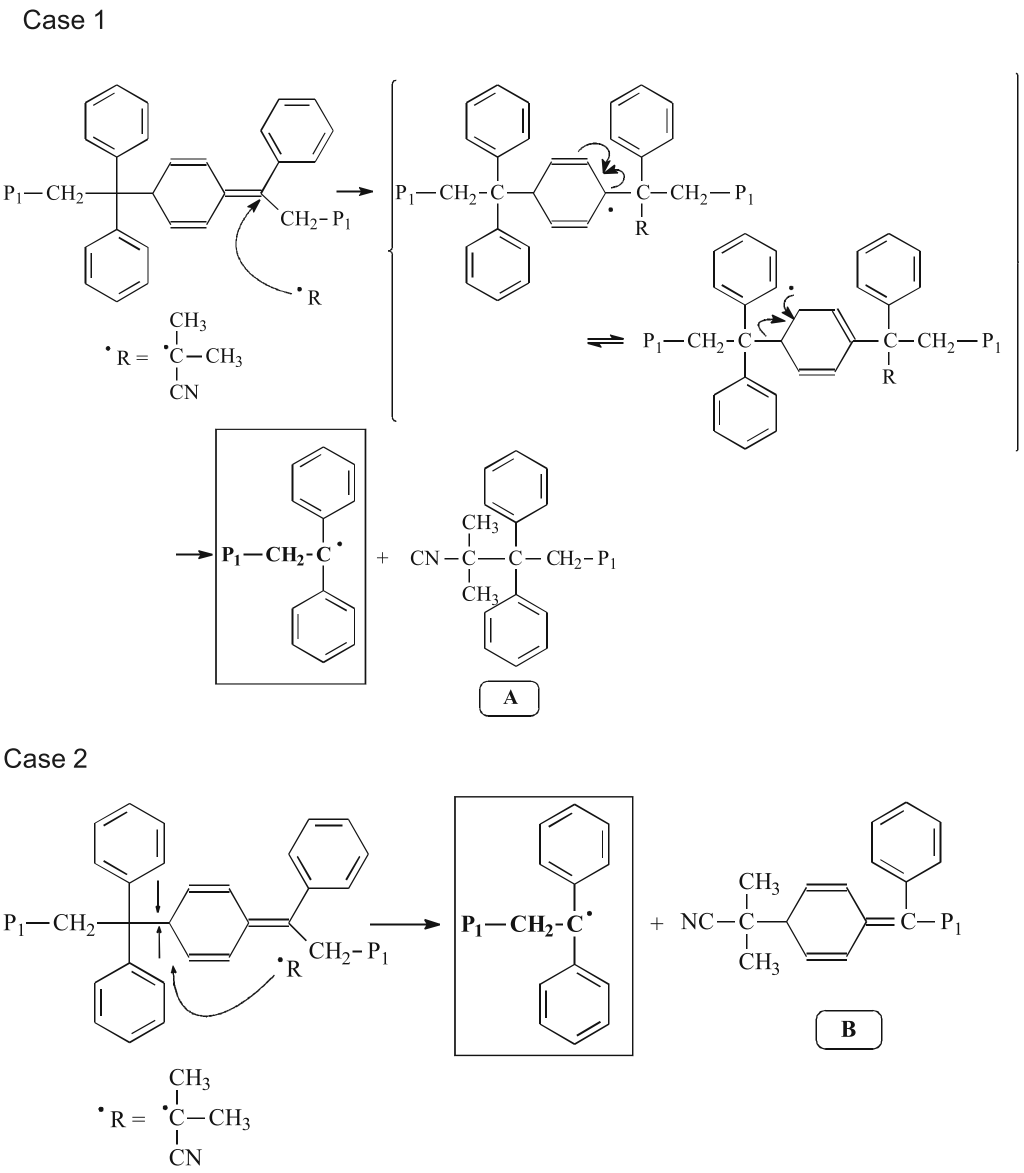


Chart 3. Possible mechanisms for the attack of radicals on the semiquinoid unit in the precursor polymers.

the reaction (cf. Fig. 3(A)) the conclusion is straightforward that the semiquinoid structure is the point along the precursor chain where radicals attack and subsequently initiate chain scission.

The final reaction mixture after duration of 70 h was fractionated by means of preparative SEC in order to isolate the high molecular weight fraction (the range is indicated in Fig. 3(A)) for subsequent analysis of its structure by NMR spectroscopy. Two different mechanisms might be considered for the attack of radicals on the semiquinoid structure as illustrated in Chart 3. Both mechanisms lead to different end products (A or B) and hence, it should be possible to differentiate, provided structural analysis by means of ^{1}H-NMR (Fig. 4) and ^{13}C-NMR (Fig. 5) is sensitive enough. In order to allow a better assignment of peaks additional H, C-cosy experiments as well as ^{13}C-NMR experiments with DEPT were carried out. Results of these experiments are put together in Table 1 where, in order to avoid too much information, only peaks are included appearing after the model reaction. Note, the attack of isobutyronitrile radicals on the semiquinoid unit in the precursor polymer can lead to a variety of possible structures (A–F) containing DPE units as summarized in Charts 3 and 4.

The multiplet at about 7 ppm in the aromatic region of the ^{1}H-NMR spectra (cf. Fig. 4, spectrum B) originates in the case of the PMMA–DPE copolymer from the phenyl group of DPE units. The ^{1}H-NMR spectrum of the high molecular weight fraction of the reaction product shows two new signals at 7.37 and 7.39 ppm, which were assigned by means of H- and C-COSY as well as ^{13}C-NMR DEPT experiments as CH from phenyl groups. This result confirms that the semiquinoid structure is broken-up by the attack of radicals.

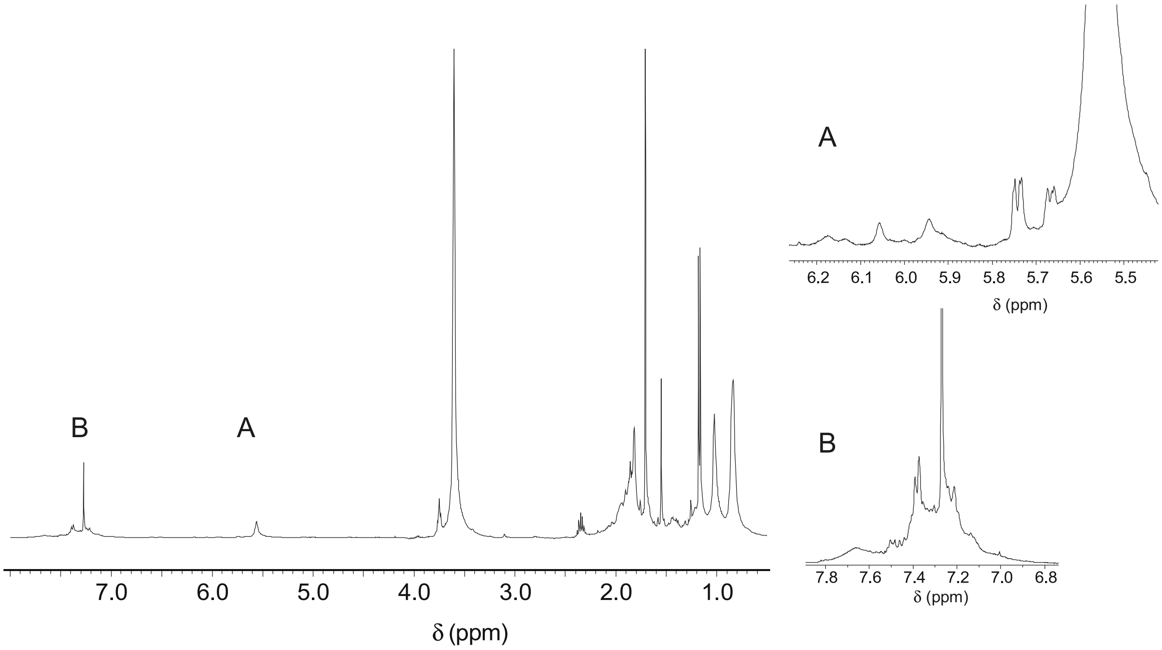


Fig. 4. 400-MHz ^{1}H-NMR spectra (chloroform at 27 °C) of the high molecular weight fraction of the reaction product of the precursor polymer after reaction with AIBN at 60 °C in THF for 70 h; spectra A and B on the right side are magnifications of the corresponding regions marked in the entire spectrum (left side).

Signals between 5 and 6 ppm have been assigned already earlier [15] either to olefinic protons of the semiquinoid structure or to terminal methine protons arising from disproportion termination between MMA ended radicals. In the spectrum of the reaction product new peaks appear in this region (cf. Fig. 4, spectrum A). These signals may arise according to the possible reaction pathways as depicted in Charts 3 and 4 from different structures that is either structure D (cf. Chart 4) or structure B (cf. Chart 3). To estimate the chemical shift of the terminal methine proton of structure D a model compound, methyl-2-ethyl-2-methyl-4,4-diphenyl-3-butenoate, can be used. The chemical shift of the terminal methine proton in the ^{1}H-NMR spectra was found at 6.03 ppm [27], which corresponds well with that of 6.06 ppm observed in the spectrum depicted in Fig. 4. Although it was not possible, neither with H, C-COSY nor with DEPT experiments, to get additional information the presence of molecules with structure D in the reaction mixture can very likely be deduced. But that means not at the same time the presence of molecules with structure B

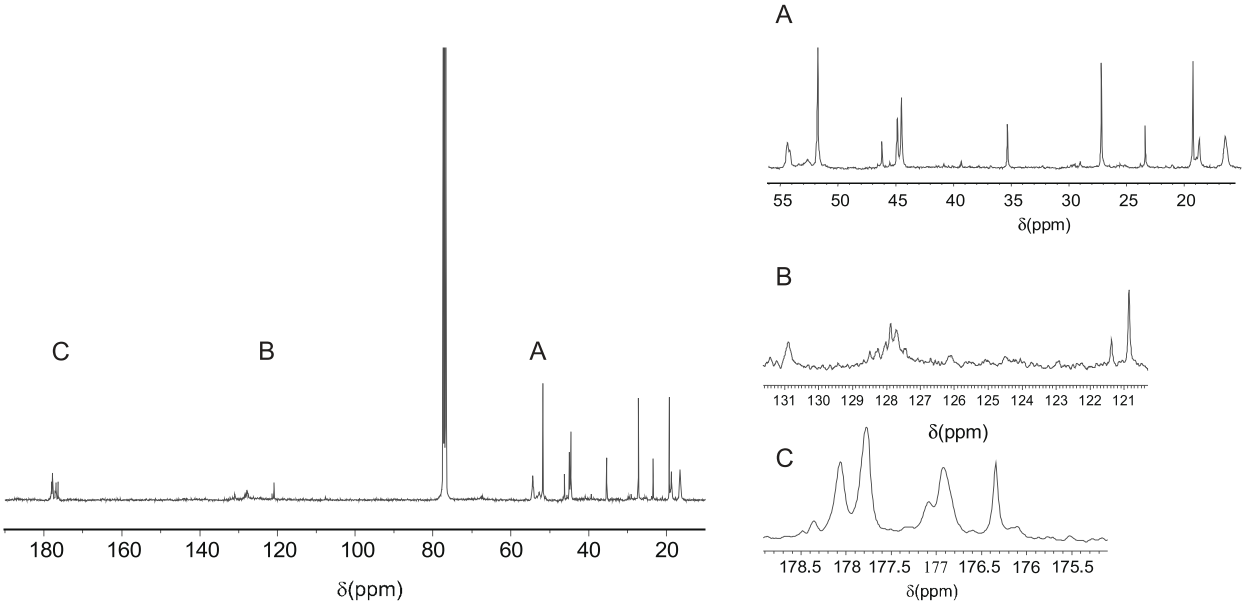


Fig. 5. 400-MHz ^{13}C-NMR spectra (chloroform at 27 °C) of the high molecular weight fraction of the reaction product of the precursor polymer after reaction with AIBN at 60 °C in THF for 70 h; spectra A and B on the right side are magnifications of the corresponding regions marked I the entire spectrum (left side).

Table 1
Summary of the new peaks appearing in ^{13}C and ^{1}H-NMR spectra of the precursor polymer after the reaction with AIBN (THF, 60 °C, 70 h)

New peaks at δ (ppm)	DEPT results	Coupled with peaks of ^{1}H-NMR at δ (ppm)	Assignment
^{13}C-NMR			
19.2	CH_3	Doublet at 1.18 and 1.16	CH_3 from AIBN; structure F
23.4	CH_3	1.55	CH_3 from AIBN; structure B
35.3	CH	Multiplet at 2.3	
39.3	C		
40.8	C		
46.2	C		
120.9	C	Corresponding to nitrile groups	CN from AIBN; structure F or B
121.4	C		
127.5	CH	7.1–7.5	Aromatic protons
127.9	CH		
128.0	CH		
128.3	CH		
128.5	CH		
130.9	CH		
176.3	C		
^{1}H-NMR			
1.16	CH_3	19.2	CH_3 from AIBN; structure F
1.18	CH_3		
1.41	Only intensity is changed		
1.55	CH_3	23.4	CH_3 from AIBN; structure B
1.71			Impurity: THF
2.16	Only intensity is changed		
2.3 Multiplet	CH	35.3	?
3.75	C	≈176	Modified $COOCH_3$; structure F
5.56			?
5.67 Doublet			Ha and Hb on B
5.75 Doublet			Hd and Hc on B
5.94			?
6.06			Olefinic H on D
6.52			?
7.37	CH	≈127	Aromatic protons
7.39			

(cf. Chart 3 and Fig. 5) can be excluded due to the arguments presented already in the preceding publication for the analysis of the NMR spectra of the precursor polymer [15]. The tacticity of the polymer chain and the chirality of the MMA-units complicate the detailed analysis and also, some signals of protons of the semiquinoid structure could be hidden. The ^{1}H-NMR spectrum (Fig. 4) shows two signals (‘multiplets’) between 5.6 and 5.8 ppm and an intense signal between 5.5 and 5.6 ppm (cf. spectrum A in Figs. 4 and 6). At a glance the peaks between 5.6 and 5.8 ppm could be considered as doublet of doublets. But both the asymmetry and the different intensities contradict this assumption. The proper peak assignment is denoted in the formula inserted into Fig. 6 whereby this assignment corresponds basically to that of the protons of the semiquinoid structure as described in Ref. [28] for the α,p-dimer of 2-methyl-1,1-diphenylpropyl radicals. Possible hidden peaks are indicated by dotted lines.

New signals of methyl protons appear as doublet at about 1.1 ppm and two single peaks at 1.55 and 1.71 ppm. The peak at 1.71 ppm can be assigned to traces of THF. According to H, C-COSY as well as DEPT experiments, the three peaks at 1.16, 1.18 and 1.55 ppm arising from CH_3 groups. These signals can be due to isobutyronitrile radicals as result of either combination termination (cf. Chart 4, structure F) or due to direct attack upon the semiquinoid structure (cf. Chart 3, structure B). The assignment of these signals to structure F is supported by results obtained for deuterated PMMA prepared in bulk polymerization initiated with AIBN at 60 °C [29]. The signal of the protons in the terminal isobutyronitrile group splits into two peaks due to the adjacent asymmetric carbon atom in the PMMA chain and hence, it forms a doublet, with signals at 1.23 and 1.31 ppm. In the case of structure F the distance between the chiral carbon and the isobutyronitrile protons is enlarged by one diphenyl methylene group and hence, this coupling constant is expected to decrease. Thus the signals at 1.16 and 1.18 ppm observed in the reaction products might corresponds to the doublet of the CH_3 groups according to structure F. The signal at 1.55 ppm arise from molecules possess structure B where the influence of the chiral center in the PMMA backbone on protons of the isobutyronitrile group is completely screened as the distance between both structural elements is too large and both CH_3 groups are magnetically equivalent. Thus, this region of the ^{1}H-NMR spectrum of the reaction product (cf. Fig. 4) reveals the

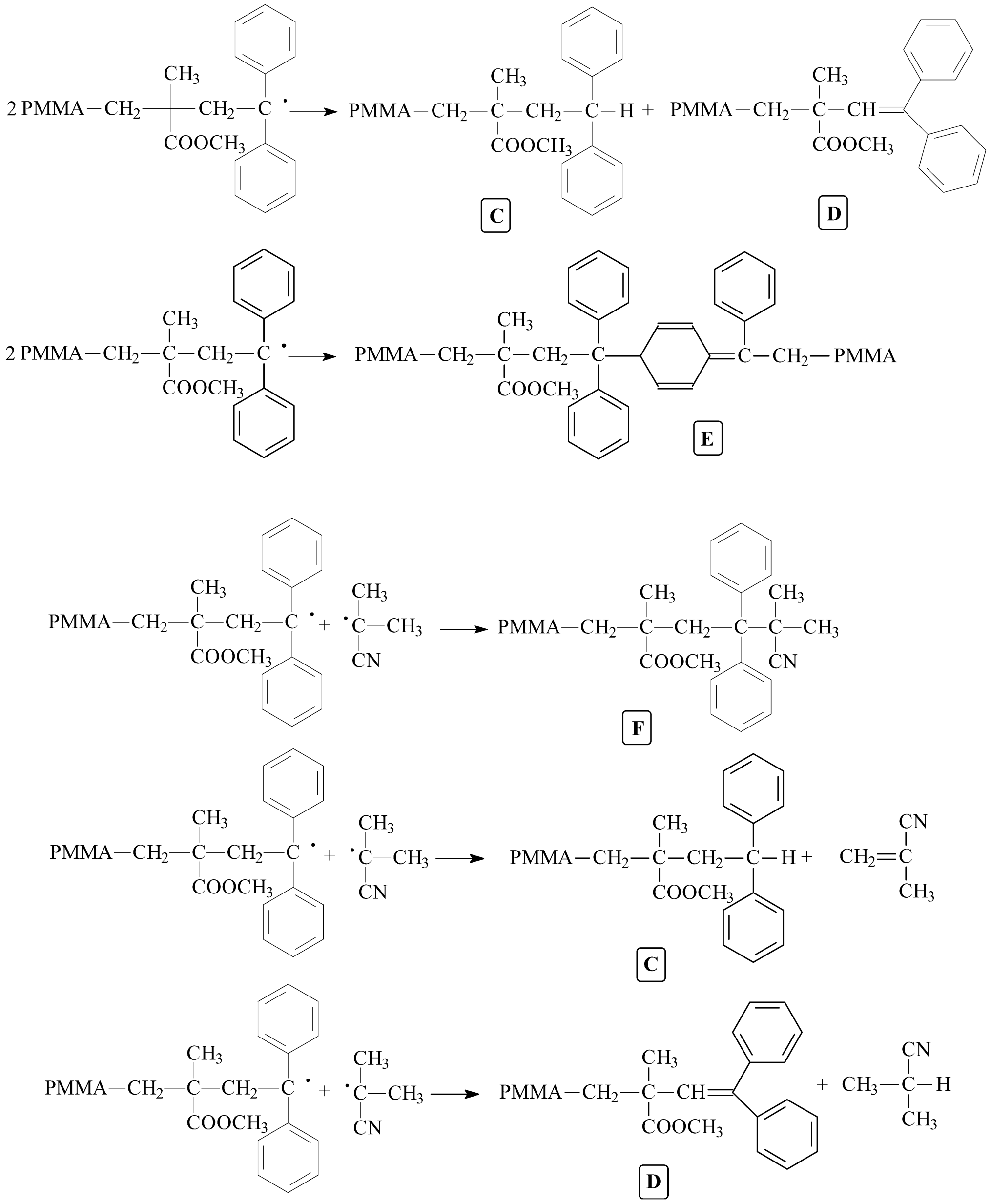


Chart 4. Possible reactions of the polymeric radical terminated with DPE and relating possible terminal structures.

presence of molecules with both structure B and F. Moreover, the ^{13}C-NMR spectrum (cf. Fig. 5) shows two signals at 120.9 and 121.4 ppm, which correspond to the nitrile group. This means that AIBN initiator-fragments are present in two different structural units, which are very likely structures B and F (cf. Charts 3 and 4).

In summary, the NMR investigations strongly indicate that the reaction product of the DPE-containing precursor polymer with AIBN is a mixture, which contains molecules with structures B, D and F (cf. Charts 3 and 4). The formation of structure B suggests that the attack of radicals upon the semiquinoid structure takes place at the weak σ-bond between the two DPE units according to the mechanism 2 as proposed on Chart 3. Under the chosen conditions during the model reaction (high concentration of mobile isobutyronitrile radicals) the probability is very low that two remaining DPE-ended radicals terminate with each other to yield again a precursor polymer. The termination with an isobutyronitrile radical is much more likely leading to either structure D or F (cf. Chart 4).

These conclusions based on the above model reaction can be used to deduce a reasonable mechanism for the second stage polymerization as is depicted in Chart 5. The conditions during the model reaction and the second stage polymerization differ only with respect to the initiator concentration and the presence of a polymerizable monomer. The polymerization reaction starts conventionally by initiator decomposition and addition of monomer molecules to primary radicals. Subsequently the addition of monomer molecules is continued until a DPE-containing precursor

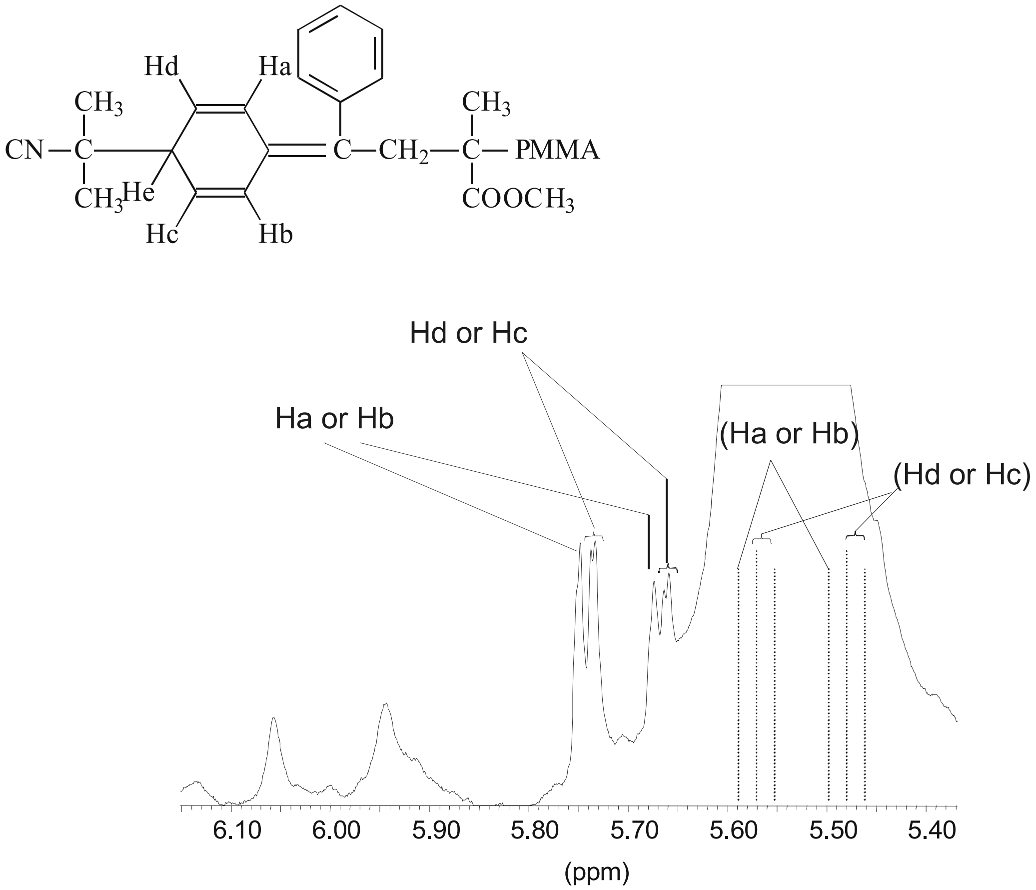


Fig. 6. ^{1}H-NMR spectrum of the semiquinoid protons of the high molecular weight fraction of the reaction product of the precursor polymer after reaction with AIBN at 60 °C in THF for 70 h (cf. Table 1).

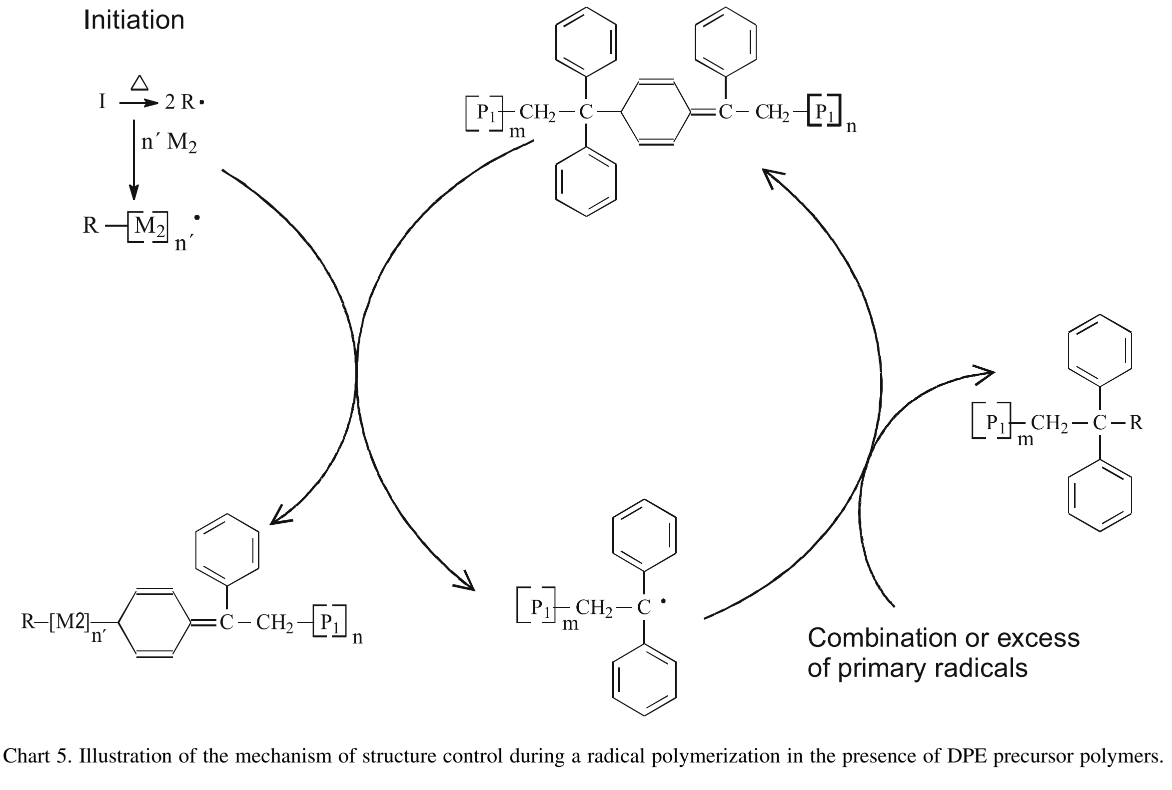


Chart 5. Illustration of the mechanism of structure control during a radical polymerization in the presence of DPE precursor polymers.

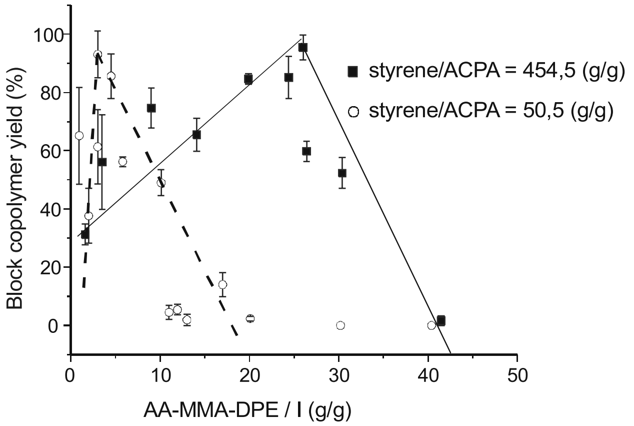


Fig. 7. Block copolymer yield between a hydrophilic precursor polymer made of acrylic acid, methyl methacrylate and DPE (AA–MMA–DPE) and styrene during an aqueous heterophase polymerization with 4,4′-azobis(4-cyanopentanoic acid) (ACPA) as initiator (I) in dependence on the precursor polymer to initiator ratio for two different monomer to initiator ratios (each experiment was repeated four times; lines are just for guiding the eyes).

polymer is met. After the attack of the growing radical on the semiquinoid structure at least two possibilities exist depending on the particular conditions with respect to the concentration ratios of all active partners (initiator, monomer, and precursor polymer). If the initiator concentration is high in comparison to the PMMA–DPE copolymer, side reactions between the polymeric, DPE-terminated radical and primary radicals are favored as illustrated in Chart 3, case 2. Contrary, if the PMMA–DPE copolymer is in excess in comparison with AIBN radicals, the recombination reaction between two DPE terminated polymeric radicals becomes more and more likely. If however a monomer molecule reacts with one of the DPE-terminated radicals similar to the equation described by case 2 in Chart 3 (that is the radical ending with a cyclohexadienyl moiety and the isobutyronitrile radical is replaced by a monomer molecule) block copolymer formation takes place. Of course, block copolymer formation occurs as well if instead of a primary radical (isobutyronitrile radical) a growing chain attacks the α,p-dimer unit of the precursor polymer. Note, only termination of two DPE-ended radicals leads to the recovery of the precursor polymer and preserves the ability to structural control and block copolymer formation. Only if at the end of the second stage polymerization enough precursor polymer molecules are left can a third polymerization with structural control be started. Also note, according to the presented mechanism each α,p-dimer unit that is each precursor polymer molecule allows at maximum the formation of only one diblock copolymer molecule and hence, there is obviously no chance to get multi block copolymers, but mixtures of different copolymers instead.

In order to illustrate this possibility of structural control in radical polymerization by means of a practical example a second step styrene polymerization under heterophase condition using a hydrophilic precursor polymer prepared by copolymerization of MMA and AA in the presence of DPE was carried out. In consideration of the stabilizer properties of the precursor polymer, this polymerization leads to surfactant free block copolymer dispersions as described in Ref. [14]. Fig. 7 highlights in a very condensed form the most important features. Note, that the block copolymer yield was determined by precipitation and dissolution in selective solvents as described in Section 2. These results clearly show that block copolymer yield can be as high as 95% and that the block copolymer yield strongly depends on the ratio precursor polymer to initiator as well as on the ratio monomer to initiator. These dependencies can be explained easily with mechanism depicted in Chart 5. If the initiator is in excess in comparison to the precursor polymer side reactions between the polymeric DPE-terminated radical and primary radicals are favored. So, the available concentration of precursor polymer for block copolymer formation decreases. In the opposite case where the precursor polymer concentration is high in comparison to the initiator concentration the recombination reaction between two DPE-ended polymeric radicals becomes likely. Besides the effect of decreasing the polymerization rate an increasing precursor polymer concentration should lead to high block copolymer yields. But surprisingly, both curves depicted in Fig. 7 exhibit a rather sharp maximum. This effect is attributed to the particular conditions during the aqueous heterophase polymerization in presence of the hydrophilic precursor polymer, which is-due to its composition-surface active. Thus, at higher concentrations of the precursor polymer a point will be reached where the particle interface is completely covered and hence the remaining precursor polymer stays in the continuous aqueous phase. The semiquinoid structure of such precursor molecules can easily be attacked by primary radicals or, in less extent, also by water-soluble oligomers, leading to an effective decrease in the concentration of initiator and subsequently also to a decrease in the block copolymer yield. The maximum values of the block copolymer yields in Fig. 7 correspond obviously to optimum precursor to initiator ratios with regard to both the formation and stabilization of polymer particles and the block copolymer yields. Moreover, such a behavior indicates that the particle water interface and the amount of adsorbed precursor polymers play a crucial role in block copolymer formation. This is a direct consequence of the particular heterophase polymerization technique employed where radical formation takes place in the aqueous phase and the polymerization reaction occurs mainly inside the monomer swollen polymer particles. Thus, the radicals, either primary or oligomeric ones, must pass through the particle water interface where they meet with a high probability of precursor polymers and may start block copolymer formation.

In summary, the experimental results presented reveal that the α,p-dimer structure in the DPE containing precursor polymers is unable to decompose thermally at temperatures between 60 and 100 °C but it is split by the attack of free radicals. This kind of induced decomposition, which can also be considered as a special kind of chain transfer, is the reason for structural control during radical polymerization in the presence of precursor polymers prepared in the presence of DPE. The applicability of this method is not restricted to a special kind of precursor polymer that is hydrophobic as well as hydrophilic precursor polymers can be employed thus allowing to apply the method in aqueous but also hydrophobic polymerization media. The formation of block copolymers is possible to a high extent if optimized conditions with regard to initiator, precursor polymer, and monomer concentration are fulfilled during the second stage polymerization.

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