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Polymer 43 (2002) 7231–7241

polymer

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Structural control in radical polymerization with 1,1-diphenylethylene. 1. Copolymerization of 1,1-diphenylethylene with methyl methacrylate

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Received 16 July 2002; received in revised form 13 September 2002; accepted 18 September 2002

Abstract

The role of 1,1-diphenylethylene (DPE) in radical emulsion polymerization of methyl methacrylate is investigated. The presence of DPE causes a strong decrease in both the rate of polymerization and the molecular weight. According to the results of structure analysis by means of MALDI-TOF mass spectrometry, UV–vis spectroscopy, and ^{1}H–NMR spectroscopy, DPE is incorporated in the copolymer chain exclusively as a reactive recombinant α,*p*-dimer, underlining the peculiar role of DPE in radical polymerizations. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Emulsion polymerization; 1,1-Diphenylethylene; Copolymer structure

1. Introduction

Contrary to anionic [1–3] and cationic [4–10] polymerizations, the role of 1,1-diphenylethylene in radical polymerization is still not yet understood in all details today. 1,1-Diphenylethylene (DPE) is well known for its inability to undergo homopolymerization [11], but it can participate in radical copolymerizations [12–21]. The participation of DPE in radical polymerization leads to the formation of stable DPE radicals (Scheme 1) by resonance stabilization of the radical by the two phenyl groups and a strong steric hindrance for the addition of any other monomer. Thus, DPE has drastic effects in radical polymerization.

In order to understand the influence of monomer structure and radical stability on free radical copolymerization, DPE was frequently chosen as a model monomer. Copolymerizations of DPE with various vinyl and acrylic monomers like acrylonitrile (AN) [12,22], methacrylonitrile (MAN) [12,22], methyl acrylate (MA) [18], methyl methacrylate (MMA) [18], acrylamide [22], styrene [13] and substituted butadienes [18] have been studied. The calculated reactivity ratios of DPE with almost all comonomers confirmed the impossibility of DPE to homopolymerize. In case of copolymerization with AN, MAN and acrylamide, the reactivity ratios of DPE are very close to zero [18,13]. These results confirm that DPE acts as retarder during radical copolymerizations and hence, DPE was also frequently used in radical polymerization in order to control the molecular weight [20].

Recently, DPE gained interest again as its utilization in aqueous heterophase polymerization allowed the preparation of surfactant-free block copolymer latexes with high solids content, which can be applied as superb binders for coatings [23–26]. The synthesis was carried out like a one pot synthesis but with consecutive addition of monomers, and indications for a controlled polymerization reaction were described. The two steps, for better academic analysis, can also be timely and spatially separated. In a first step, a mixture of acrylate or methacrylate monomers with acrylic acid is polymerized in water in the presence of DPE without addition of surfactant. The amount of monomers in the mixture is adjusted in such a way that water-soluble, DPE-containing polymers with pronounced amphiphilic character result. In a second step hydrophobic monomers are added, and the polymerization is conducted in the presence of the first step product as a polymeric stabilizer and control agent with regard to the formation of block copolymers. However, the mechanism of this kind of polymerization,

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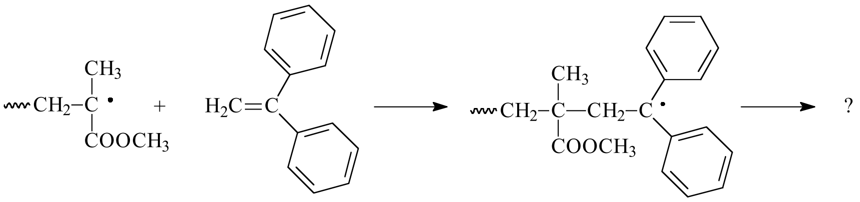
PII: S0032-3861(02)00676-6



Scheme 1. Formation of PMMA-chain with a terminal DPE radical.

especially the formation of block copolymers, is rather unclear although the block structure of the copolymers obtained at the end of the second step polymerization was proved.

More recently DPE was used to carry out controlled radical polymerization of styrene and other vinyl monomers in bulk [27,28]. The resulting DPE precursor copolymers were subsequently employed to prepare block copolymers. The authors describe the molecular structure of the DPE copolymers as a result of combination termination either between two polymeric radicals terminated with DPE (leading to so-called α,α-dimers) or between DPE and styrene radicals [27]. The formation of α,α-dimers as termination products is also claimed for the copolymerization between MMA and DPE [28]. However, the mechanism of the control of radical polymerization by DPE-copolymers is not yet clear. The main reason for the lack of a satisfying mechanism is caused by the lack of information with regard to the structure of the DPE-containing precursor polymer. For instance in Ref. [28] the authors discuss three alternatives, however, without presenting direct analytical evidence for one or the other possibility. In particular the authors propose that structural units composed of either α,α-dimers of DPE or structures resulting from head-to-head addition between a DPE-ended and principal radicals are labile units along the precursor copolymer chains, which are responsible for block copolymer formation during the second step polymerization. As third possibility is the participation of a DPE-ended polymer chain, which is formed after disproportionation termination during the first polymerization, discussed as active center for the control during the subsequent polymerization.

The aim of this contribution is to clarify the real polymerization scenario of radical copolymerizations with DPE. Special emphasis is placed on investigations of the copolymer structure in order to understand the role of this copolymer precursor during the second step polymerization, which will be treated in forthcoming contributions.

2. Experimental section

Reaction calorimetry. The reaction calorimetry was carried out batchwise in a reaction calorimeter RM2-S from ChemiSens (Lund, Sweden) with a 200 ml reactor equipped with a stainless steel stirrer and a heating facility through the reactor bottom. Water (105 g), MMA (20 g), DPE (1.05 g) and a solution (15.25 g) of 25% NH_3 in water were added to the reactor and heated up to 70 °C. After thermal equilibration the reactor was calibrated with an input of 2 W of electric power. The reaction was started after re-equilibration by injecting aqueous initiator solution (1.12 g ammonium peroxo disulfate (APS) in 4 g of water).

MMA–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 from a Seral purification system (PURELAB Plus™) with a conductivity of 0.06 μS 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.

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

The latex obtained 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 as long as the conductivity of the filtrate was constant. The polymer was isolated by freeze-drying. After freeze-drying, the solid obtained was purified by dissolution–precipitation cycles. After dissolution in tetrahydrofuran (THF), the THF solution was poured into an excess of methanol. The polymer was isolated by filtration, washed with methanol, and dried. This purification was repeated using cyclohexane instead of methanol as the precipitant.

PMMA reference polymer synthesis. The synthesis and purification of the PMMA reference-polymer followed the same procedure as above without DPE.

Size exclusion chromatography (SEC). SEC was

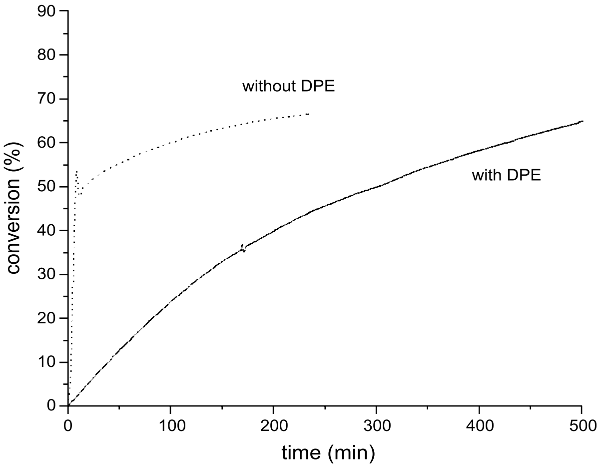


Fig. 1. Conversion-time plot of emulsifier-free emulsion polymerization of MMA in presence and absence of DPE.

performed using a P1000 pump from thermo separation products (TPS), equipped with a RI-detector (Shodex RI-71) and UV1000 detector ($\lambda = 260$ nm, TPS). SEC was operated at 30 °C with distilled 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).

MALDI-TOF mass spectrometry. MALDI-TOF MS was carried out with a Kratos Maldi III from Shimazu Europa GmbH (Duisburg, Germany) using a nitrogen laser source ($\lambda = 337$ nm), a positive polarity and 20 kV acceleration voltage. The measurements were performed in the reflector mode. For the PMMA–DPE copolymer, 2′,4′,6′-trihydroxyacetophenone monohydrate as matrix and sodium chloride as salt were used to form the adduct. For the measurement of the PMMA reference-polymer, 2,5-dihydroxybenzoic acid was used instead of 2′,4′,6′-trihydroxyacetophenone monohydrate as matrix. The polymer solutions were prepared in THF with a concentration of 10 mg/ml. The matrix and the salt were dissolved in THF as well (20 and 10 mg/l, respectively). The matrix, polymer and salt were mixed in a ratio polymer/matrix/cation = 1:2:1. About 1 μl of this solution was disposed on the sample holder and dried in air at room temperature. The equipment was calibrated using a two-point calibration with 2,5-dihydroxybenzoic acid and insulin as standards.

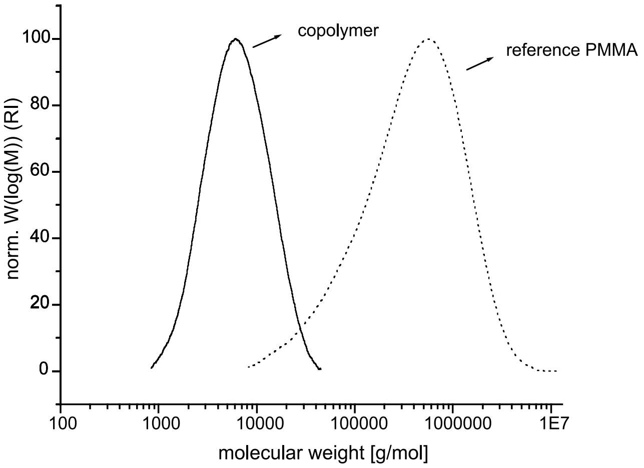


Fig. 2. Molecular weight distribution of PMMA prepared by emulsion polymerization in presence and absence of DPE.

Fourier transform infrared spectroscopy. Infrared spectra were collected at room temperature on a BioRad 6000 FT-IR spectrometer equipped with a single reflection diamond ATR cell.

UV–vis spectroscopy. UV-spectra were recorded at room temperature with a Uvikon 931 spectral photometer from Kontron Instruments S.P.A, Milan, Italy in acetonitrile.

NMR. ^{1}H spectra were obtained on a Bruker DPX-400 spectrometer in $CDCl_3$ at room temperature. ^{1}H chemical shifts were referenced to TMS via the residual nondeuterated solvent signal at $\delta = 7.23$ ppm.

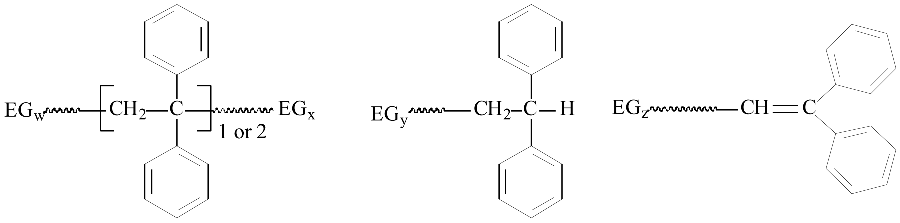
3. Results and discussion

3.1. Polymerization kinetics in presence of DPE

In order to investigate the influence of DPE on the polymerization kinetics the conversion was followed by reaction calorimetry. Since polymerization in the absence of DPE was much too fast for the resolution of the calorimeter, especially during the initial stage in presence of SDS, another recipe than that employed for the synthesis of the DPE-containing copolymer was used for all further analytical investigations (Section 2). To get sufficient resolution, MMA was polymerized in a batch, surfactant-free emulsion polymerization with 2.6 mol% APS as initiator in the presence as well as in the absence of DPE at 70 °C. Both reaction profiles are depicted in Fig. 1. The initial stage of the reaction in the absence of DPE is extremely fast even under these throttled conditions, but the polymerization rate clearly decreases in the presence of DPE.

As expected, the presence of DPE also influences the molecular weight. The chromatograms depicted in Fig. 2 show a strong decrease in the molecular weight, i.e. $M_w = 7.9 \times 10^3$, $M_n = 4 \times 10^3$ and $M_w = 3.1 \times 10^6$, $M_n = 3.4 \times 10^4$ g mol^{-1} in presence and absence of DPE, respectively. Note, these are the cumulative molecular weight distributions and averages of the final polymers prepared in the presence of SDS.

Both the calorimetry and the molecular weight data show that DPE takes part in radical MMA polymerization in a way that is comparable to that of degradative chain transfer agents [29] as it causes a drastic decrease in both the rate of polymerization and the average degree of polymerization. From these results the conclusion can be drawn that with a



Scheme 2. Possible structures of PMMA–DPE copolymers (Eg$_{w-z}$ denote different end groups resulting from initiation of chain growth).

terminal DPE-radical the kinetic chain is stopped because it is obviously unable to restart chain growth. With regard to the structure of these copolymers it can be concluded that DPE is either present as an end group (as a result of chain transfer or termination by disproportionation) or within the chain as a dimer (as a result of termination by recombination).

3.2. *The structure of the MMA–DPE copolymer*

Scheme 2 shows possible structures of the DPE-containing copolymer, as deduced from the kinetic data and GPC investigations. To identify the real structure FT-IR spectroscopy, MALDI-TOF spectrometry, UV–vis spectroscopy, and ^{1}H NMR spectroscopy were employed.

The FT-IR spectra compared in Fig. 3 show for both products the characteristic bands of PMMA at 1720 cm^{-1} (stretching of carbonyl group C=O) and 1238 cm^{-1} (the stretching of ester group C–O), but for the copolymer in addition two bands at 700 and 775 cm^{-1}. These bands can be assigned to monosubstituted aromatic groups, which are in the particular case the result of backbone vibrations with participation of both phenyl rings. Compared to the spectrum of pure DPE, these bands are shifted thus indicating that these bands arise from copolymerized DPE but without any possibility to decide between the above structural possibilities. Furthermore, the concentration of DPE in the copolymer is obviously quite low.

MALDI-TOF mass spectrometry was performed on these products in order to get information concerning the composition of end groups. MALDI-TOF mass spectrometry is a powerful tool to investigate the chemical structure of a polymer [30,31], at least of the parts that fly under the particular experimental conditions. Limitations may arise due to fragmentation and discrimination, which are observed especially in case of samples with broad molecular weight distributions [32,33]. Thus, results of MALDI-TOF measurements with respect to overall molecular weight have to be discussed in addition to the GPC data, which represent the whole sample.

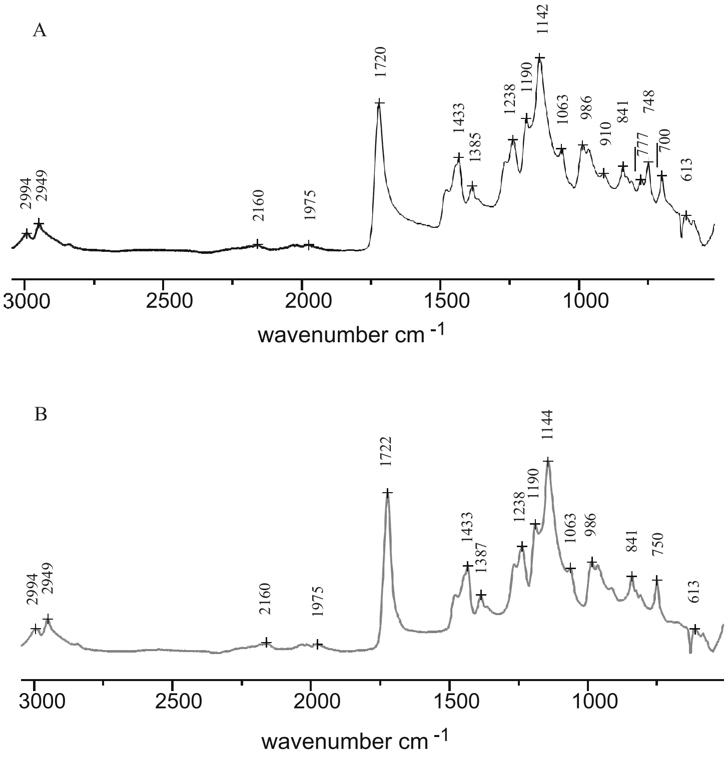


Fig. 3. FT-IR spectra of DPE–MMA copolymer (A) and PMMA reference homopolymer (B).

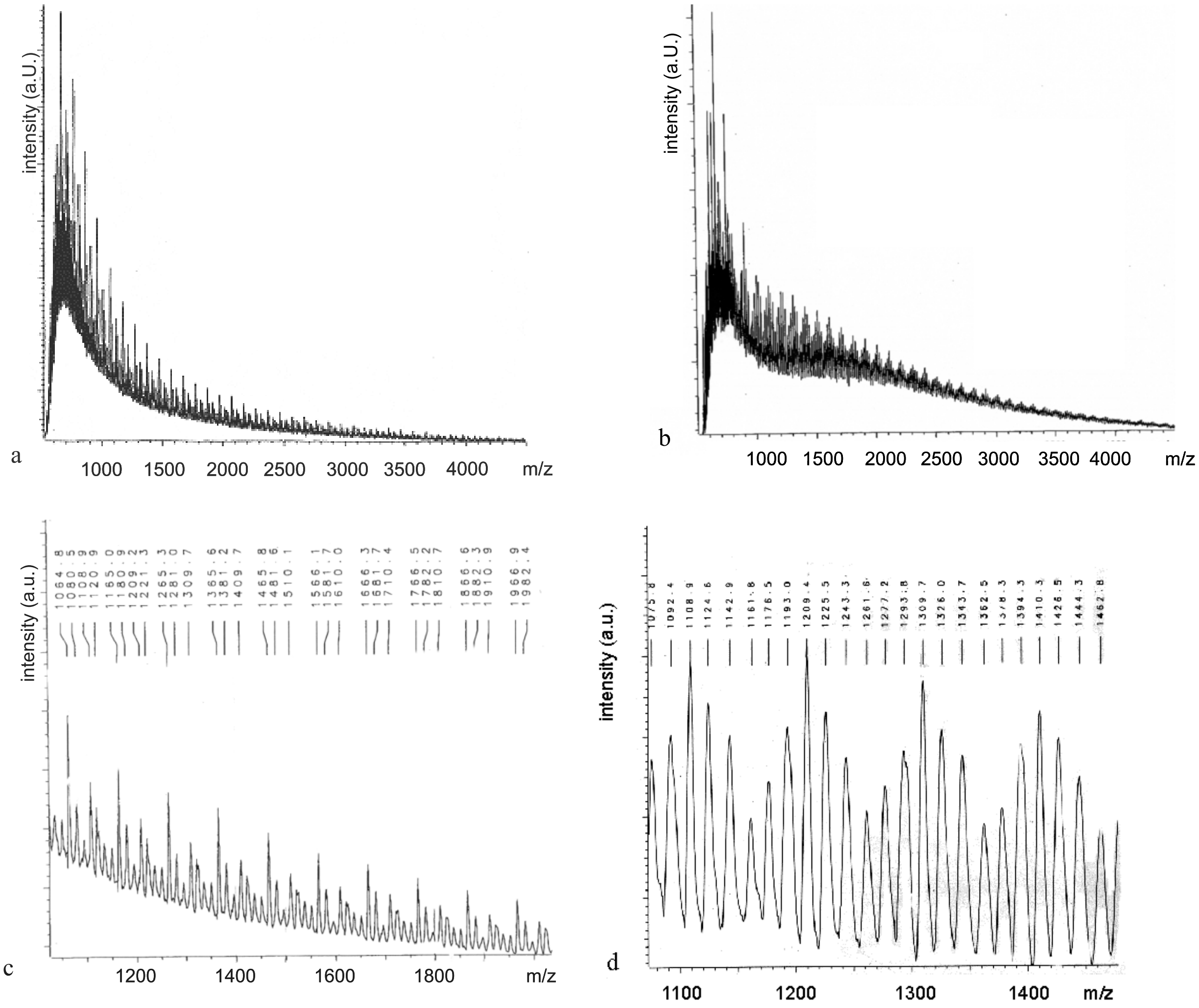
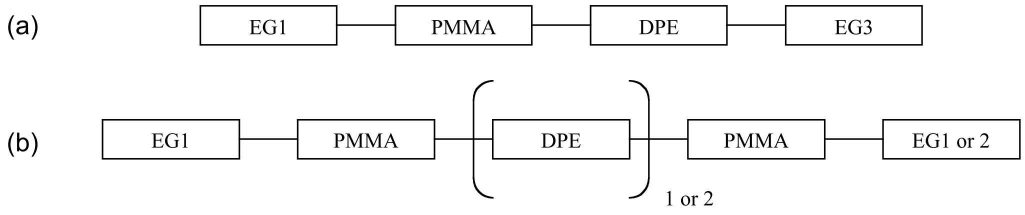


Fig. 4. MALDI-TOF mass spectra for the reference PMMA (a,c) and the MMA–DPE copolymer (b,d); a, b whole spectra and c, d zooms into particular mass ranges.

The MALDI-TOF spectra for both the homo- and the copolymer show two common features. First, the mass gap between two peaks of equal intensity is 100 g mol^{-1}, which corresponds to the molecular weight of the MMA unit. Second, both spectra exhibit a variety of side-peaks around the main peaks, thus indicating a chemical variety of end group pairs. However, closer inspection elucidates that the end group pattern is different in both cases. Furthermore, the comparison with the GPC data reveals that during MALDI-TOF measurements fragmentation and/or discrimination takes place for both samples Fig. 4.

Due to the similar 100-spacing pattern, the MALDI-TOF spectra show that the DPE–MMA copolymer exhibits neither a statistical nor a block-like composition with high DPE content but that DPE is only present as punctual groups. Thus, these data confirm the above conclusion regarding the possible structure as depicted in Scheme 2. These possibilities are again listed in Scheme 3, placing special emphasis on the terminal groups and residual masses that can be expected. Again, two models are likely (a) chain termination by disproportionation and (b) chain termination by combination. In this sense EG1 and EG2 denote end groups arising from the initiation reaction whereas EG3 arises from disproportion. Note that the end group pattern of



Scheme 3.

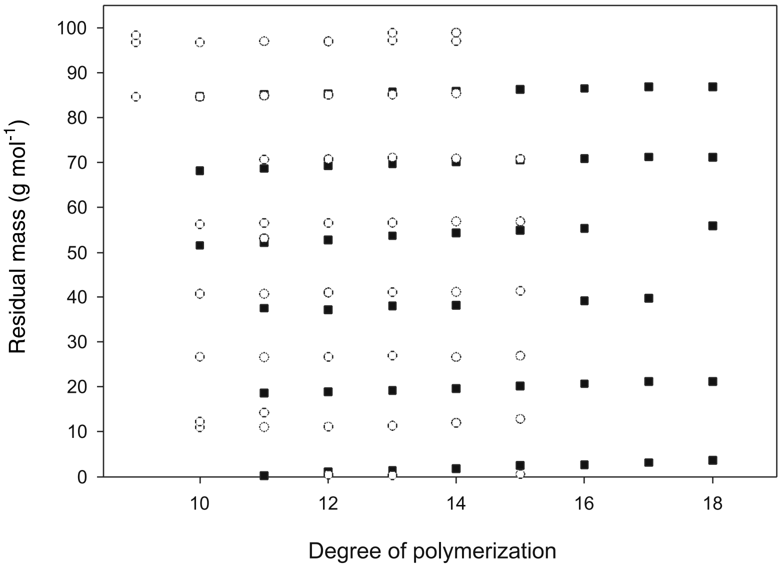


Fig. 5. Residual masses as a function of the degree of polymerization of the DPE–MMA copolymer (■) (cap-polymer) and the PMMA homopolymer (○).

polymers prepared by aqueous emulsion polymerization initiated with peroxodisulfates is characterized by more than only sulfate groups because a variety of side reactions take place. Typically, for a polymerization initiated with peroxodisulfates, these are side oxidation reactions which lead to the formation of hydroxyl end group and carboxylic end group [34–36].

For the evaluation of the MALDI-TOF data only integer values of the molecular weights will be considered. The mass to charge ratio *m*/*z* of the detected ions corresponds to the number of *m*/*z* of repeating MMA units (100 Da) plus *m*/*z* of the ionizing ion (natrium, 23 Da) and *m*/*z* of both end groups. The mass to charge ratio of both end groups will be hereafter named *residual mass*. The residual mass can be calculated for all peaks as follows (Eq. (1)):

$$M_r = z\left[\left(\frac{m}{z}\right)_{\text{detected}} - \left(\frac{m_{\text{ion}}}{z}\right)\right] - nM_{\text{monomer}} \qquad (1)$$

The plot of the different residual masses as a function of the degree of the polymerization (Fig. 5) reveals that each chain length is represented by least six and eight separate peaks for the reference polymer and the copolymer, respectively. The difference in the patterns of the residual masses between reference polymer and copolymer is due to the action of DPE and thus, is a further indication of its strong influence on polymerization kinetics (Tables 2 and 3).

Table 1 summarizes possible end group combinations and the theoretical corresponding residual masses, which serve as base for the following detailed discussion. The counterions of the sulfate and carboxylic end group can be of various origin such as K^+ from the reactor material, NH_4^+ from the initiator, Na^+ from the surfactant or the reactor material, and H^+ from ion exchange during the purification of the polymers. As the samples have been extensively cleaned before characterization (Section 2) the probability of the occurrence of the various cations decreases in the following order: $H^+ > NH_4^+ > Na^+ \gg K^+$.

The experimental setup used allows discrimination of

Table 1
Theoretical residual masses ($m_{\text{res,t}}$ in g mol^{-1}) for the various possible end groups (EG) and their origin

$m_{\text{res,t}}$	EG	Origin
96	$-SO_4^-$	Initiation with sulfate ion radicals
17	$-OH$	Initiation with hydroxyl radical or hydrolysis of a polymer chain ending in a sulfate end group Initiation with hydroxyl radical formed during peroxodisulfate decomposition [35]
130	$-OO^-$	Oxidation of a hydroxyl end group by peroxodisulfate or its decomposition products
1	$-H$	Initiation by hydrogen radical transfer from a water molecule Termination by H transfer from disproportion reaction
179	$-CH{=}C(Ph)_2$ (DPE)	Termination by disproportion reaction of a polymer radical ending in DPE
181	$-CH_2-CH(Ph)_2$ (DPE–H)	
99	$-CH{=}C(CH_3)COOCH_3$ (MMA)	Termination by disproportion of a polymer radical ending in MMA
99	$-CH_2-C(COOCH_3){=}CH_2$ (MMA–H)	
101	$-CH_2CH(CH_3)COOCH_3$ (MMA–H)	

Note, this analysis does not consider carboxylic groups as the result of ester hydrolysis which can occur all along the chain. These groups have a formal residual mass of 85 g mol^{-1} per hydrolyzed unit.

Table 2
Experimental residual mass ($m_{\mathrm{res,e}}$), number of peaks (n) and assignment of end group combinations (EG1, EG2) for the reference PMMA homopolymer

$m_{\mathrm{res,e}}$ (g mol^{-1})	n	EG1	EG2
1.5 ± 0.5	3	H	H
		MMA	H
		MMA−H	H
		OOH	OOK
		$OONH_4$	OONa
11.6 ± 0.7	6	SO_4NH_4	SO_4H
		SO_4H	OH
		MMA	SO_4NH_4
26.7 ± 0.2	6	SO_4NH_4	SO_4NH_4
		SO_4H	OOH
41.0 ± 0.2	6	SO_4Na	SO_4Na
		OOK	OOK
56.7 ± 0.2	6	SO_4Na	SO_4K
		OONa	H
		OONa	MMA−H
70.8 ± 0.2	5	SO_4K	SO_4K
		SO_4Na	OONa
		OOK	H
		OONa	OH
		MMA−H	OOK
		MMA	OOK
85.0 ± 0.3	6	SO_4K	$OONH_4$
		SO_4NH_4	OOK
		OONa	OOH
		OOK	OH
96.9 ± 0.2	6	SO_4H	MMA−H
		SO_4H	H
		$OONH_4$	$OONH_4$
		MMA	SO_4H

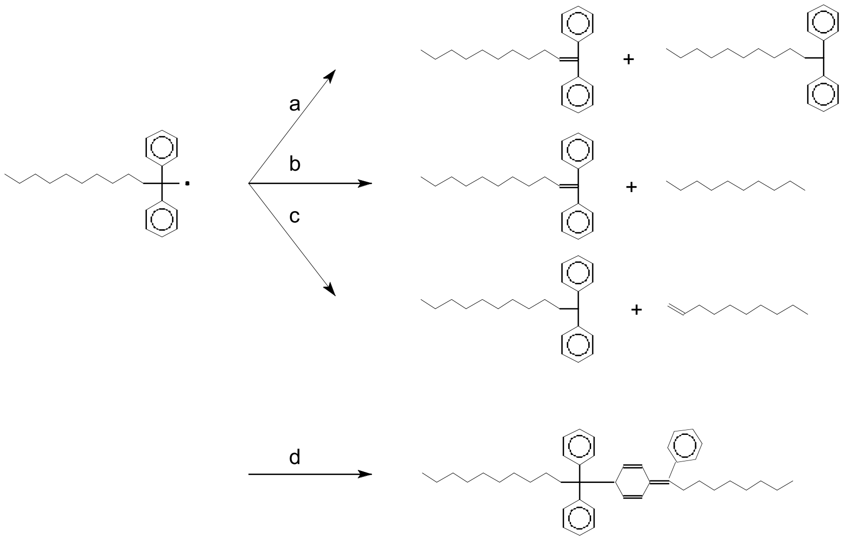
two structures which are separated by two mass units. Note that the assignment is not unequivocal because a particular experimentally determined residual mass could correspond to more than one end group combination. The assignment of observed residual masses for the reference PMMA homopolymer to possible end groups is summarized in Table 2. Under these particular conditions, where no DPE is present the observed eight peaks may correspond to 75 theoretical end group combinations.

The data summarized in Table 2 prove the occurrence of initiating side reactions also for MMA emulsion polymerization as it was earlier already detected for styrene emulsion polymerization started with peroxodisulfate [35].

For the corresponding analysis of the copolymer with DPE, the following assumptions were used. Firstly, DPE influences essentially the kinetics of the chain reaction. This means that all polymer molecules are directly or indirectly influenced by DPE. Secondly, DPE ended radicals are unable to chain growth reactions via propagation. Thirdly, in the presence of DPE the normal chain transfer reactions are only of minor importance. In order to facilitate the analysis of the MALDI-TOF spectra the reaction pathways leading to dead polymer chains as illustrated in Scheme 4 might be useful.

The analysis requires the consideration of three species that are molecules with either none, one, or two DPE units. The DPE molecule can be formally considered as end groups and hence, one DPE and two DPE molecules per chain increase the residual mass by 180 and 360 g mol^{-1}, respectively. Furthermore, if there is only one DPE molecule per average polymer reaction a–c are possible pathways leading to end group combinations, where one arises from initiation and the other from termination by disproportionation. On the contrary, molecules with two DPE units (pathway d) as the result of combination termination contain always two endgroups arising from chain initiation. Note, for products formed via pathways a–d the possible overall number of end group combinations is 95. These results of the assignment of end groups are summarized in Table 3.

In order to get information about possibly real end group



Scheme 4. Termination path ways of DPE ended radicals (concerning the structure that results from path way d).

Table 3
Experimental residual masses ($m_{res,e}$), number of peaks (n) and assignment of end group combination (EG1, EG2) for various MMA–DPE copolymers according to Scheme 4

		2 DPE		1 DPE		0 DPE	
$m_{res,e}$ (g mol^{-1})	n	EG1	EG2	EG1	EG2	EG1	EG2
2.1 ± 1.1	8	SO_4H	$OONH_4$	SO_4Na	MMA	MMA	H
		SO_4NH_4	OOH	SO_4Na	MMA–H	MMA–H	H
19.9 ± 1.0	8	SO_4NH_4	$OONH_4$	none	none	MMA–H	OH
		OOH	OOH			SO_4Na	MMA
38.3 ± 1.0	6	$OONH_4$	OOH	none	none	none	none
53.9 ± 1.6	8	$OONH_4$	$OONH_4$	SO_4H	DPE	OONa	MMA
		SO_4H	SO_4H			OONa	MMA–H
70.0 ± 1.1	9	SO_4NH_4	SO_4H	none	none	OOK	MMA
						OOK	MMA–H
85.9 ± 0.8	9	SO_4NH_4	SO_4NH_4	none	none	none	none
		SO_4H	OOH				

combinations in the DPE–MMA copolymers it is necessary to compare the experimental residual masses with that of assumed copolymer structures. The most probable copolymer structure is that which end group combinations fit to the experimentally determined pattern. The data summarized in Table 3 clearly show that only the calculated end group combinations assuming two DPE units per molecule can match the experimental pattern of the residual masses. The assumed mixture of molecules with none or one DPE unit per molecule does not fit on the experimental data, as end groups with residual mass of 38.3 and 85.9 g mol^{-1} cannot be realized.

These results clearly lead to the conclusion that the DPE–MMA copolymers have a structure with always two DPE units linked together as connecting groups due to recombination of two growing chains each terminated with DPE-radicals. Structures with a single DPE molecule, as were postulated in previous publications [27], in the chain can be, at least according to these MALDI-TOF results, excluded.

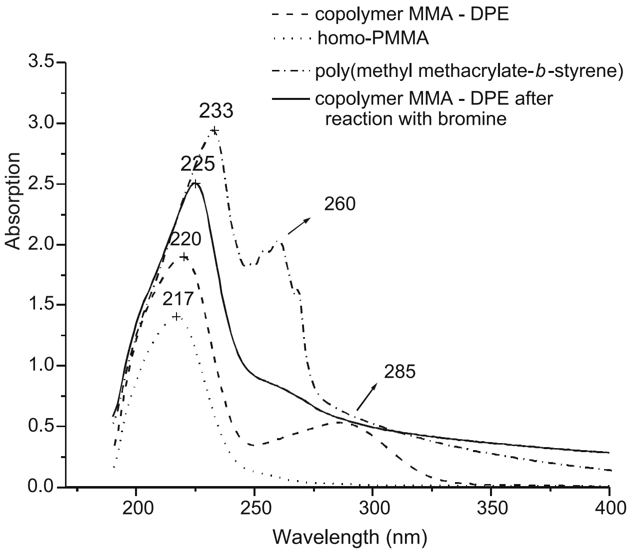


Fig. 6. UV–vis absorption spectra in acetonitrile solution for various polymers under consideration.

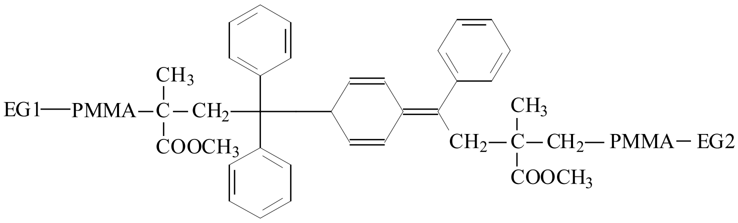
MALDI-TOF analysis only allows one to determine the mass, but not unambiguously the chemical structure of polymer end groups. Consequently other characterization methods have to be utilized in order to learn more about the structure and in the particular case more about the DPE-dimers which are obviously active in further radical polymerization.

The ultraviolet–visible (UV–vis) absorption spectrum of the copolymer shows a broad absorption band between 250–330 nm with a maximum at 285 nm (Fig. 6). It is noteworthy to mention here that also other DPE containing copolymers such as with hydroxyethyl methacrylate or with (butyl methacrylate)-*co*-(acrylic acid) exhibit similar absorption spectra. In comparison, a block copolymer, poly(methyl methacrylate-*b*-styrene), with 300 MMA units, 40 styrene units, and a single DPE connecting group exhibits a sharp maximum at 260 nm. This comparison suggests that the recombinant dimer has a more conjugated structure, which is responsible for the bathochromic shift in the UV–vis absorption spectrum. Just for the sake of completeness, the reference homo-PMMA shows no absorption at all in this spectral range.

Moreover, the MMA–DPE copolymer causes discoloration of a bromine solution, which changes the UV–vis absorption spectrum (Fig. 6). Note, the discoloration of a bromine solution was not observed in case of the homo-PMMA or an anionic copolymer of styrene and DPE synthesized by anionic polymerization [37,38]. This result clearly proves the presence of reactive double bonds in the copolymer.

The presence of reactive double bonds in the MMA–DPE copolymer points strongly towards the formation of a semi-quinoid structure as shown in detail in Scheme 5.

Considering the bulkiness of DPE radicals, rearrangement during combination, leading to the semi-quinoid structure seems very plausible. Note this is in contradiction to a previously discussed structure of DPE-copolymers [27,



Scheme 5. Semi-quinoid structure as result of recombination of two DPE-terminated radicals.

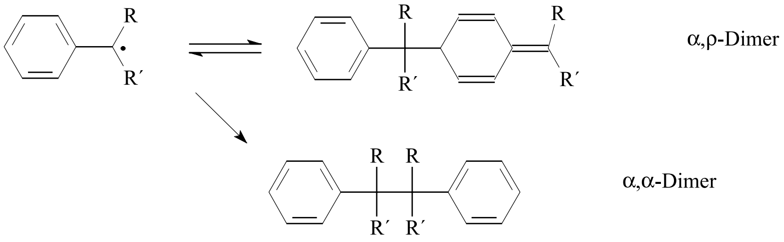
28], but in agreement with results in classical organic chemistry. For instance, the rearrangement of triphenylmethyl radicals to an analogous quinoid structure instead of to hexaphenylethane was the key to solve the so-called hexaphenylethane riddle [39,40]. Furthermore also various substituted benzyl radicals recombine to corresponding quinoid structures [41–45]. Beckhaus et al. [42–44] investigated especially the tendency of benzyl radicals to form α, α-dimers or α,*p*-dimers and defined a steric parameter as an expression of steric hindrance of the substituent R in PhCRR′. According to the work of Beckhaus termination by recombination (or dimerization) should preferably lead to α,*p*-dimers (Scheme 6).

Further proof for the quinoid structure as formed in reaction pathway d of Scheme 4 or as depicted in detail in Scheme 5 comes from UV–vis spectroscopic results obtained for the recombination product of phenyldialkylmethyl radicals, where an absorption of the α,*p*-dimers between 260 and 270 nm was observed [41]. The observed slightly bathochromic shift in the UV–vis absorption for the corresponding α,*p*-dimer unit in the DPE–MMA copolymers (Fig. 6) can be easily explained by the action of the neighboring ester groups.

An analogous structure for PMMA–DPE copolymers was already proposed in 1959 by Kice and Taymoorian [16] for free radical bulk polymerization of MMA and DPE initiated with AIBN. These authors concluded, based on investigations with UV-spectroscopy and comparison with model compounds such as 1-benzylidene-2-cyclopentene, that at least some of the DPE units in the copolymer have the semi-quinoid structure. Contrary to our results, Kice and Taymoorian [16] also reported a termination by disproportionation between DPE ended and MMA ended polymeric radicals. The MALDI-TOF data presented here exclude this possibility at least for the present reaction conditions of aqueous emulsion polymerization.

Further support for the quinoid recombinant dimer structure was obtained from ^{1}H–NMR spectra (Fig. 7). In comparison with the reference polymer, no differences in the PMMA region between 1 and 4 ppm are visible whereas in the region between 5 and 7 ppm new signals appear. Beside the multiplet at 7.6–6.8 ppm due to the aromatic protons of the DPE units, the spectra contain singlets at 6.18, 6.16, 5.77, 5.46, 5.44 and 5.41 ppm. These signals can be attributed to methylene protons of the cyclohexadiene structure or—as an alternative—to unsaturated MMA end groups [46,47]. The signals of terminal methylene protons from disproportionation termination between two MMA-radicals are observed at 6.16 and 5.41 ppm. The signal at 5.41 ppm splits into two signal due to the tacticity of the terminal diad.

The methylene protons on the cyclohexadiene structure in positions 3 and 5 (Hb and Hc) are magnetically nonequivalent. In fact, the presence of the proton Ha causes a limitation of the free rotation around the σ-bond of the cyclohexadiene structure. The signals of Hb and Hc are split due to spin–spin coupling with the protons Hd, Ha and He, Ha, respectively. Theoretically, the signals corresponding to the protons Hb and Hc should be observed as doublets of doublets. Moreover, the signal corresponding to the proton Hc should split into two peaks due to the influence of the tacticity of the polymer chain and the chirality of the MMA unit. For these reasons, the protons Hd and He are magnetically also nonequivalent. As Hd and He are coupled with Hb and He, respectively, their signals should appear as two doublets. Moreover, the proton He is in the same plane as the polymer chain and its signal should be influenced by the tacticity of the polymer chain. Therefore, the signal corresponding to He should split into two peaks. One can expect two doublets of doublets and two doublets. The observed signals in the region 5–7 ppm were assigned with the help of some model substances, in particular the dimer of 2-methyl-1,1-diphenylpropyl radicals [48]. The peak assignments are denoted in Fig. 7B and C).



Scheme 6. Dimerization of disubstituted benzyl radicals according to Beckhaus et al. [42].

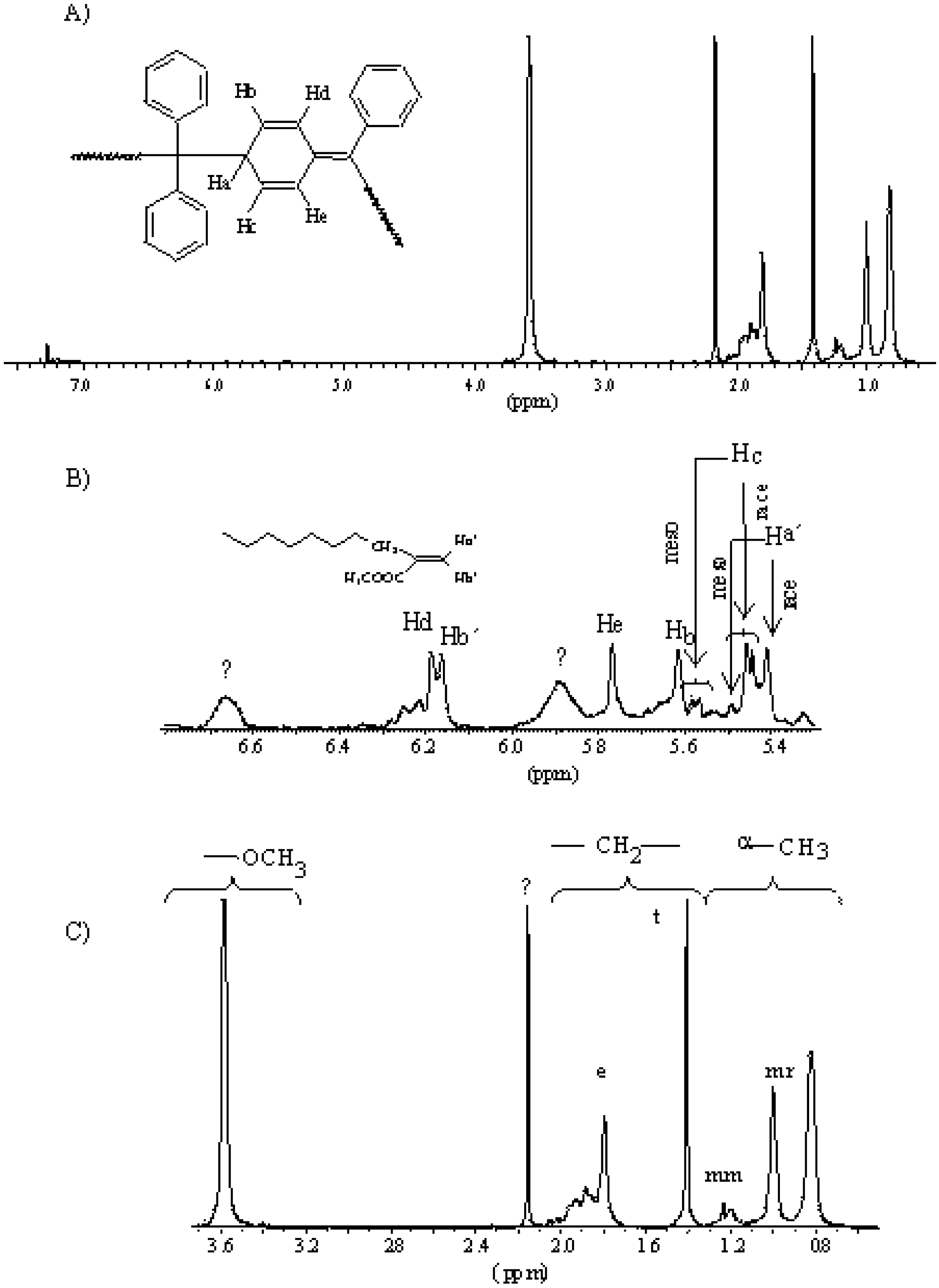


Fig. 7. (A) ^{1}H–NMR spectra of DPE–MMA copolymers; (B,C) magnification and peak assignment.

In conclusion, DPE participates in radical polymerization of MMA in a very special way. From a kinetic point of view it behaves virtually like a degradative chain transfer agent. That is, it causes a decrease in both the rate of polymerization and the molecular weight compared with PMMA homopolymerization. Analysis of the copolymer structure with MALDI-TOF mass spectrometry, UV–vis spectroscopy, and ^{1}H–NMR spectroscopy reveals that DPE is exclusively present in the copolymer chains within the chain in the form of a dimer with semi-quinoid structure (Scheme 5). Thus, the DPE-terminated polymeric radicals stop the kinetic chain because of their low reactivity. Obviously, based on the above results the only subsequent reaction is a combination with a second DPE terminated polymeric radical via formation of the semi-quinoid structure.

The chemical peculiarity of this semi-quinoid structure is that it can be effectively be reopened by a second radical process, thus resulting in the formation of block copolymers via reactive chain transfer. This, however, will be analyzed in detail in a forthcoming publication.

Acknowledgements

The authors gratefully acknowledge the Max Planck Society and BASF Coating AG for financial support.

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