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Block Copolymers by Using Combined Controlled Radical and Radical Promoted Cationic Polymerization Methods

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Summary

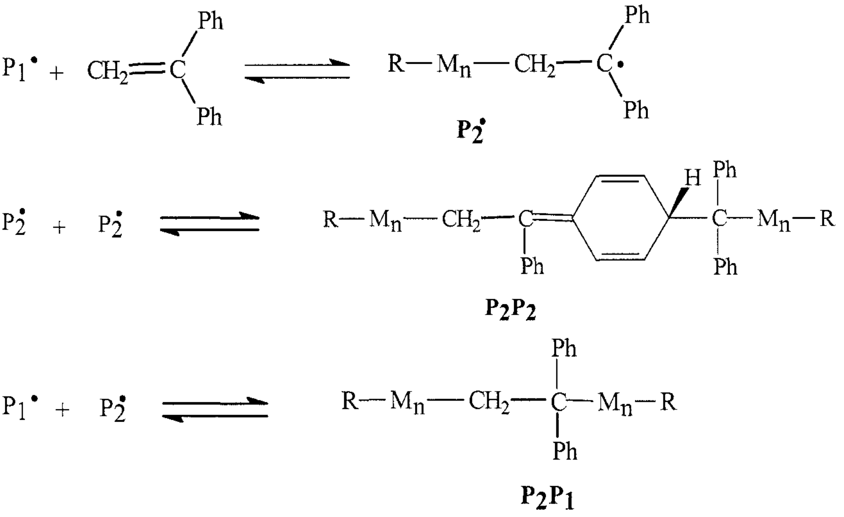
A novel synthetic procedure for the preparation of block copolymers based on the combination of diphenylethene (DPE) mediated controlled radical polymerization and radical promoted cationic polymerization is described. In the first step, the controlled polymerization of styrene (St) and methyl methacrylate (MMA) in presence of DPE yields polymers with various structures of diphenylethyl units in the main chain. Upon heating these prepolymers undergo scission to give polymeric radicals. Oxidation of these radicals by onium salts such as diphenyliodonium heaxfluorophosphate ($Ph_2I^+PF_6^-$) and *N*-ethoxy-2-methylpyridinium hexafluorophosphate ($EMP^+PF_6^-$) yields reactive cations capable of initiating cationic polymerization of cyclohexene oxide (CHO). Block copolymer structure was confirmed by IR and NMR spectral measurements and GPC analysis.

Introduction

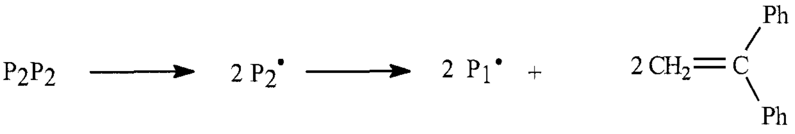
Controlled free radical polymerization has been successfully applied for the synthesis of well-defined specific polymer architectures[1]. Several methods, such as atom transfer radical polymerization (ATRP)[2], stable radical mediated radical polymerization[3] and reversible addition-fragmentation chain transfer (RAFT)[4,5] became known in the last years. Recently, a new additive was introduced for the controlled radical polymerization of numerous vinyl monomers[6,7]. The addition of 1, 1-dipenylethene (DPE) to a conventional polymerization system consisting of initiator and monomer results in a controlled behavior of the polymerization. This method overcomes some problems observed in the existing controlled polymerization methods associated with high temperature conditions, catalyst removal and limited applicability to specific monomers. Although the exact mechanism of the DPE method is not clear yet, following scheme can explain the experimental observation.

$$I \longrightarrow 2\,R^{\bullet} \tag{1}$$

$$R^{\bullet} + nM \longrightarrow \underset{P_1^{\bullet}}{R{-}M_n^{\bullet}} \tag{2}$$



For radical block copolymerization P_2P_2 (or P_2P_1) can be applied as initiator for second a monomer. P_2P_2 splits into $2P_2^{\bullet}$ radicals at higher temperature and it becomes active for further polymerization after split of DPE from $P_2^{\bullet}$ resulting $P_1^{\bullet}$ (reactions 6 and 7).



(6)

$$P_1^{\bullet} + mM_2 \longrightarrow \text{block copolymer} \tag{7}$$

In order to extend the range of monomers for the synthesis of block copolymers, transformation approach was postulated by which the polymerization mechanism could be changed from one to another, which is suitable for the respective monomers. Numerous examples of some transformation reactions combining various polymerization methods including recently developed controlled radical polymerizations have been summarized recently.[8]

It was reported that the oxidation of electron donor radicals to corresponding cations may conveniently be used to promote cationic polymerization of monomers such as epoxides, cyclic ethers, and alkyl vinylethers.[9-12] Electron donor radicals can be generated thermally, photochemically and by other means such as electron beam irradiation. The overall process may be represented by reaction (8) and useful oxidants include onium salts such as diaryliodonium salts[10, 11]. Pyridinium salts[12] of appropriate reduction potentials are also capable of participating in similar redox reactions.

$$R^{\bullet} \xrightarrow{On^{+}} R^{+} \tag{8}$$

In the present work, polymers prepared by using DPE method were used as a free radical source. Heating of these polymers in conjunction with onium salts in the presence of cyclohexene oxide (CHO) as a cationically polymerizable monomer (M_2) makes it possible to synthesize block copolymers of monomers of different chemical nature as depicted below.

$$P_2^{\bullet} \xrightarrow{On^{+}} P_2^{+} \tag{9}$$

$$P_2^{+} + M_2 \longrightarrow \text{block copolymer} \tag{10}$$

Experimental

Materials

Monomers, styrene (St), methyl methacrylate (MMA) and cyclohexene oxide (CHO), and solvent, dichloromethane were purified by conventional drying and distillation procedures. Diphenyliodonium hexafluorophosphate ($Ph_2I^+PF_6^-$)[13] and *N*-ethoxy-2-methyl pyridinium hexafluorophosphate ($EMP^+PF_6^-$)[14] were prepared as according to published methods. 1, 1-Diphenylethene (DPE) was distilled before use. 2, 2'-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol.

Homopolymerization of St or MMA by DPE Method

Bulk monomers (St or MMA) containing a known amount of AIBN and DPE in glass tubes were degassed by bubbling dry nitrogen. The tubes were then immersed in a constant-temperature bath at 80 °C. At the end of a given time the reaction mixtures were cooled to room temperature and poured into a ten fold excess methanol. The precipitated polymers were then filtered off and dried in vacou. The conversion of the polymerization was determined gravimetrically.

Promoted Cationic Block Copolymerization

Appropriate solutions of CHO in dichloromethane containing above obtained polystyrene or poly (methyl methacrylate) and onium salts were degassed and heated in a bath at 80°C. The block copolymers formed during reaction were separated from the reaction mixture by precipitation into methanol, filtered and finally dried in vacou. A conversion of CHO was determined gravimetrically after subtracting the weight of the precursor polymers. Homopoly (cyclohexene oxide) was extracted with n-hexane.

Characterization of Polymers

Molecular weight and molecular weight distribution of the polymers were determined by gel permeation chromatography (GPC) on a Waters instrument equipped with R410 differential refractometer and 600E pump using polystyrene standards. THF was used as the eluent at a flow rate of 1.0 mL/min. ^{1}H-NMR measurements were performed in $CDCl_3$ solution using a Bruker 250 MHz instrument.

Results and discussion

Poly (styrene) and poly (methyl methacrylate) possessing diphenylethyl units in the main chain were prepared by taking advantage of controlled radical polymerization using DPE as an additive. The results are shown in Table 1. As can be seen, polymers with relatively low polydispersity ($1.26 \leq M_w/M_n \leq 1.5$) were obtained. It is known[15] that triphenyl methyl radicals, produced thermally or photochemically from the related azo initiator (reaction 11), may readily be oxidized to the corresponding carbocations by onium salts having suitable redox potentials (reaction 12).

Table 1. Polymerization[a)] of St and MMA in bulk in the presence of DPE

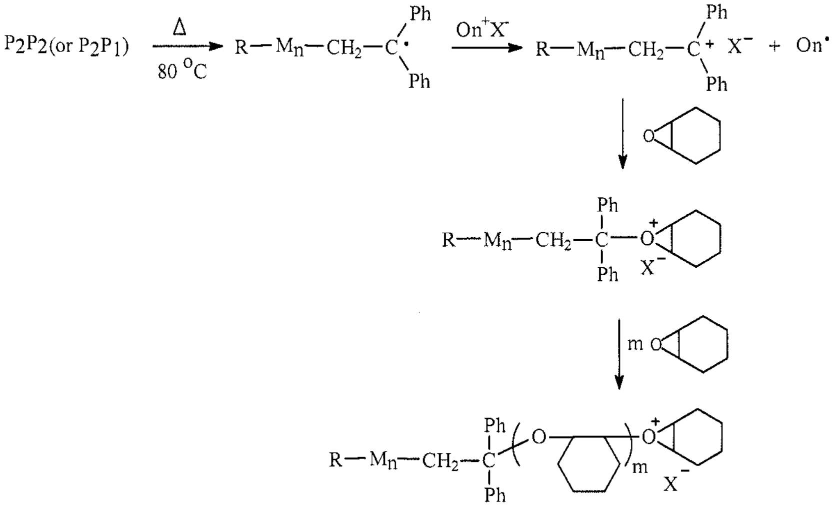
Monomer	Time (min)	Conversion (%)	$^{b)}M_n\text{x}10^{-3}$	M_w/M_n	Polymer
St	100	25	16.2	1.50	PSt-1
St	200	35	19.6	1.41	PSt-2
St	300	44	21.6	1.39	PSt-3
MMA	100	23	19.1	1.44	PMMA-1
MMA	200	35	21.9	1.37	PMMA-2
MMA	300	38	24.6	1.26	PMMA-3

[a)] Temp = 80 °C, [AIBN]/[DPE]: 1/1, [AIBN] = 2, 61 x 10^{-2} mol/L, [DPE] =2, 61 x 10^{-2} mol/L , [b)] Determined by GPC

$$Ph_3C{-}N{=}N{-}Ph \xrightarrow[-N_2]{\Delta \text{ or } h\nu} Ph_3C^{\bullet} + Ph^{\bullet} \qquad (11)$$

$$Ph_3C^{\bullet} + Ph_2\overset{+}{I}\,\overset{-}{PF_6} \longrightarrow Ph_3\overset{+}{C}\,\overset{-}{PF_6} + Ph_2I^{\bullet} \qquad (12)$$

Polymers obtained by the DPE method possess thermolabile diphenylethyl units in the main chain (structures $\underline{\mathbf{P_2P_1}}$ and $\underline{\mathbf{P_2P_2}}$) as proved by the thermolysis in the presence of radical scavengers such as 2,2,6,6-tetramethyl-piperidin-1-oxyl (TEMPO) and galvinoxyl[16]. Upon heating structurally similar polymeric alkyldiphenylmethyl radicals are expected to be formed (reaction 13). If the thermolysis is carried out in the presence of CHO and an onium salt such as $Ph_2I^+PF_6^-$ or $EMP^+PF_6^-$, the polymer attached diphenylmethyl radical is converted to the initiating cations to generate block copolymers according to the reactions 14 and 15. Typical results concerning block copolymerization via promoted cationic polymerization are presented in Table 2. It is interesting to note that the molecular weights of the block copolymers are usually lower that those of the precursor polymers. This is expected since the thermolysis of the initial polymers causes scission and polymeric radicals with shorter chain length are formed. The chain growth of the second block proceeds from the short chain cationic centers formed as a result of radical to cation transformation. A different situation was encountered in the case of free radical blocking reactions[6]. Various coupling reactions taking place during the DPE method result in the formation of block copolymers with higher molecular weights. Termination via combination may also contribute to this observation.



(13)

(14)

(15)

Table 2. Block Copolymerization$^{a)}$ of PSt and PMMA with CHO in CH_2Cl_2

Prepolymer (g/L)	Onium Salt	Time (h)	Con. (%)	$^{b)}M_n$x10^{-3}	M_w/M_n	$^{c)}$Blocking yield (%)	Composition^d PCHO (mol %)
PSt-1 (0.15)	$Ph_2I^+ PF^-_6$	7	13.52	13.7	2.08	49	12.3
PSt-1 (0.15)	$EMP^+ PF^-_6$	7	17.50	18.0	1.61	40	12.3
PSt-1 (0.15)	$EMP^+ PF^-_6$	12	28.62	13.7	1.81	46	29.3
PMMA-1 (0.07)	$Ph_2I^+ PF^-_6$	7	3.70	23.2	1.33	54	53.3
PMMA-1 (0.07)	$EMP^+ PF^-_6$	7	6.80	12.8	1.78	41	53.3
PMMA-3 (0.07)	$EMP^+ PF^-_6$	7	5.80	14.4	1.93	61	52.2

$^{a)}$[CHO] = 4, 93 mol/L, [Onium salt] = 5 x 10^{-3} mol/L, Temp: 80 °C, $^{b)}$Determined by GPC $^{c)}$Weight of block copolymer after extraction of homopolymer/ weight of block copolymer before extraction of homopolymer x 100, ^{d}Determined by NMR

The block copolymer structure was assigned by means of IR and NMR spectral measurements. IR spectra of purified block copolymers show characteristic ether bond of the PCHO segment at 1090 cm^{-1} in addition to the respective PSt and PMMA bands. The NMR spectra of the block copolymers display signals of both segments (Figures 1 and 2). Moreover, dual detection by refractive index and UV measurements provides clear evidence for the successful block copolymerization. As can be seen from Figure 3, gpc traces of PCHO-PSt block copolymer measured by UV (λ=274 nm) and refractive index appear at the same elution volume.

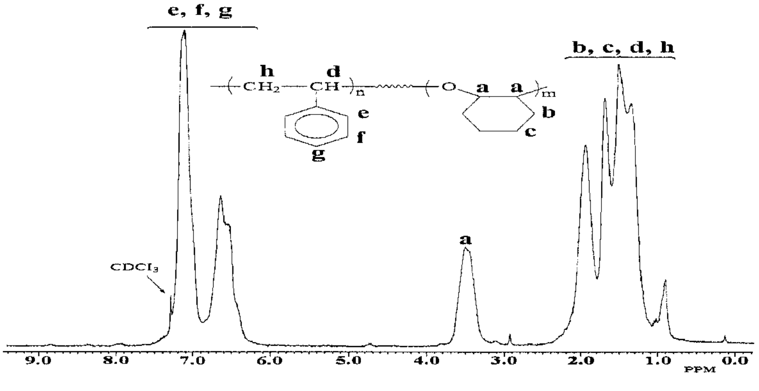


Figure 1. ^{1}H-NMR spectrum of PSt-PCHO block copolymer in $CDCl_3$.

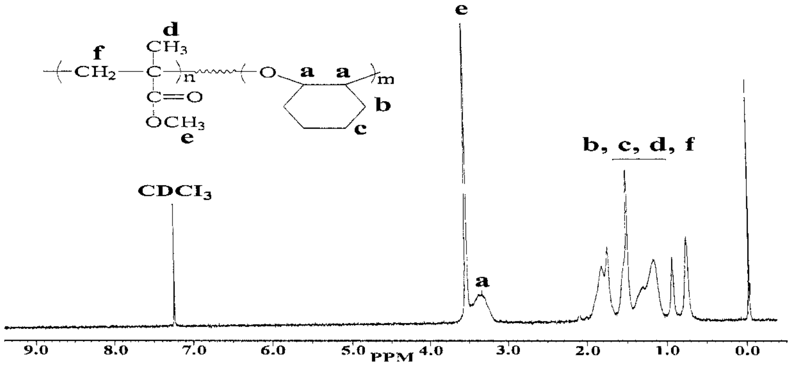


Figure 2. ^{1}H-NMR spectrum of PMMA-PCHO block copolymer in $CDCl_3$.

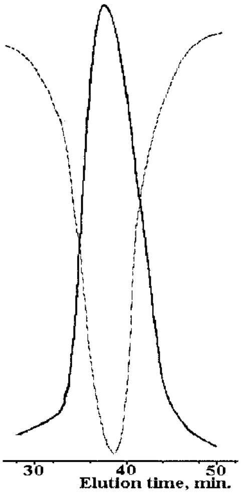


Figure 3. GPC trace of PSt-PCHO block copolymer: refractive index signal (-) and UV signal at λ= 274 nm (--)

In conclusion, although additional investigation is certainly needed to explore the generality of the method described it is clear that the combination of free radical polymerization by using DPE and free radical promoted cationic polymerization provides a versatile route for the preparation of block copolymers with different polymerizability.

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