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Dispersion redox copolymerization of methyl methacrylate with macromonomeric azoinitiator as a macrocrosslinker

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Abstract

The dispersion copolymerization of methyl methacrylate (MMA) with macromonomeric azoinitiator, MIM-400, as a macrocrosslinker initiated by the benzoyl peroxide (BPO)/*N*,*N*′dimethylaniline (DMA) coupled in water/ethanol (4/1, v/v) at 20°C was carried out to yield PEG-b-PMMA networks with labile azo linkages in the main chain. Gel fraction, swelling ratios (q_v) and the average molecular weights between junction points (M_c) values of the networks were investigated. Maximum gel fraction was obtained using 0.133 M MIM-400, 9.2×10^{-2} M BPO, 2.1×10^{-2} M DMA and 2.19 M MMA. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Dispersion redox copolymerization; Macromonomeric azoinitiator; Macroinimer

1. Introduction

Many redox pairs containing organic and inorganic components as polymerization initiator have been used successively. In these redox initiation systems, free radicals are produced by the oxidation of the substrate, which in turn initiate the polymerization. Commonly used oxidants include peroxides, persulphates, permanganates, etc. the salts of transition metals. These oxidants form potential redox systems with various reducing agents like alcohols, aldehydes, amines, amides, ketones, acids, thiols etc. for the aqueous polymerization of vinyl monomers [1–3]. In this manner, benzoyl peroxide/dimethylaniline couple is also an ideal redox pair in the polymerization of vinyl monomers. Detailed kinetic investigation of styrene polymerization by the system benzoyl peroxide/dimethylaniline was carried out at different temperatures [4–6].

Macromonomeric initiators (macroinimers; MIM) are prepared from 4,4′-dicyano-4,4′azovaleric acid, 4-vinylbenzyl chloride and polyethylene glycol (PEG) behave as macromonomers, macrocrosslinkers and macroinitiators [7–10]. Macroinimers were thermally homopolymerized and copolymerized with styrene and in both cases, gave crosslinked or branched PS-PEG block copolymers [8]. Lower initial concentration of macroinimers caused lesser yield of crosslinked polymers. The degree of swelling of the crosslinked polymers in toluene was proportional to the molecular weight of the macroinimers. Higher yield was obtained by longer polymerization time. The swelling properties in toluene or water of crosslinked polymers were proportional to the polymerization time [9]. Swelling of the networks in water was also considerable because of the hydrophilic nature of the PEG units. In gelation behavior of macroazoinimers versus PEG-macrocrosslinkers (MCR), the gelation behavior of MIM was found to be remarkably different from that of MCR [10]. In each case, gel fractions and swelling ratios of the gels kept changing with the molecular weights of the PEG sequences. Critical minimum concentrations for the onset gelation were determined as; 5, 8, 10 and 10 wt.% for MIMs containing PEG units with molecular weight 400, 1000, 1500 and 2000, and 6, 12, 18 and 19 wt.% for MCRs containing PEG units with the same molecular weights as above. Below those concentrations no network was formed. Dispersion copolymerization of styrene and MMA with macroazoinimers as macrocrosslinker and macroinitiator was studied in detail and crosslinked block copolymers were also obtained in this manner [11]. The properties of the crosslinked block copolymers and the kinetic parameters of dispersion copolymerization of MMA and St with macroazoinimers have also been discussed. In the range of medium conversions, the rate of polymerization was found to be proportional to the 1.7th and 1.6th power of MIM-400 and MIM-1500 for MMA and to the 2.5th power of MIM-400 for St, respectively.

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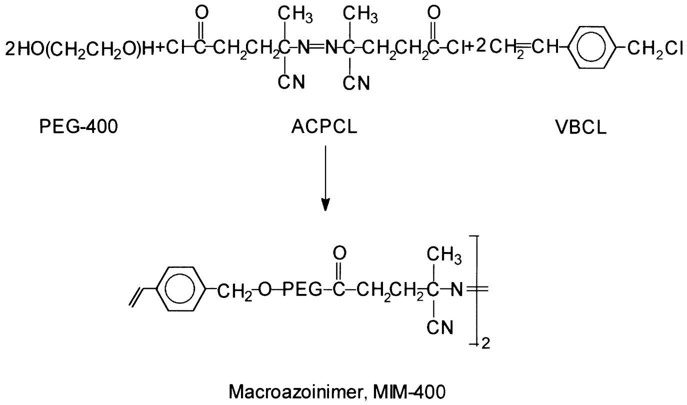


Scheme 1.

Macroazoinimers have been discussed in this article only as a macrocrosslinker. Dispersion copolymerization of vinyl monomers with macroazoinimers was carried out using external redox initiator system, benzoyl peroxide/dimethylaniline, at 20°C.

2. Experimental

2.1. Materials

Poly(azo-bis-4-vinylbenzyl ether)-400, MIM-400, was synthesized from polyethylene glycol with M_w of 400, 4,4′-dicyano-4,4′ azovaleryl chloride and 4-vinylbenzyl chloride (Scheme 1). MIM-400 was characterized by IR and NMR spectroscopy and GPC chromatography methods. Vinyl content of MIM-400 per unit was determined as 2.05 by the bromination process. These steps are indicated in detail in Ref. [10].

Analytical grade poly(oxyethylene) (PEG-400, where the number shows the molecular weight of PEG) and 4,4′-dicyano-4,4′azovaleryl chloride were used. DMA was purified by vacuum distillation in a stream nitrogen. BPO was purified twice by dissolving in chloroform followed by precipitating out by methanol. MMA was purified by the usual method. Double-distilled water and ethanol were used as polymerization medium.

2.2. Polymerization procedure

MMA was added to BPO and MIM-400, and placed in a hard glass tube, being cooled in the dry-ice methanol cooling bath [4]. A defined amount of ethanol/water (4/1, v/v) and DMA were then added. The tightly capped tube was placed in a shaker thermostated at 20°C. After 24 h, the tube content was quickly precipitated by pouring into methanol, filtered off and dried under vacuum at 25°C.

2.3. Extraction of the sol fraction

Toluene was chosen as the extraction solvent and used at room temperature. Crude gel samples was placed in excess of toluene and the solvent was replaced every other day over a period of 3 weeks until no further extractable polymer could be detected. The swollen networks were then washed several times with methanol and dried under vacuum to a constant weight at room temperature. The amount of soluble polymer in toluene solution was determined gravimetrically after evaporation and precipitation in methanol. The weight fraction of the gel, W_g was calculated as:

$$W_g = g/(g + s)$$

where g and s are the weights of extractable network and soluble polymer, respectively [12,13].

2.4. Determination of swelling ratios (q_v) of crosslinked polymers

The swelling of the cross-linked polymer samples was carried out by storing 0.2 g of the samples in 30 ml toluene for 24 h at 25°C. The swelling ratio, q_v, was calculated by the following equations [14]:

$$q_v = \frac{V_{\text{dry polymer}} + V_{\text{solvent}}}{V_{\text{dry polymer}}} = \frac{V_{\text{swollen polymer}}}{V_{\text{dry polymer}}}$$

where $V_{\text{dry polymer}}$ the volume of dry polymer and V_{solvent} is the volume of the absorbed solvent at equilibrium swelling.

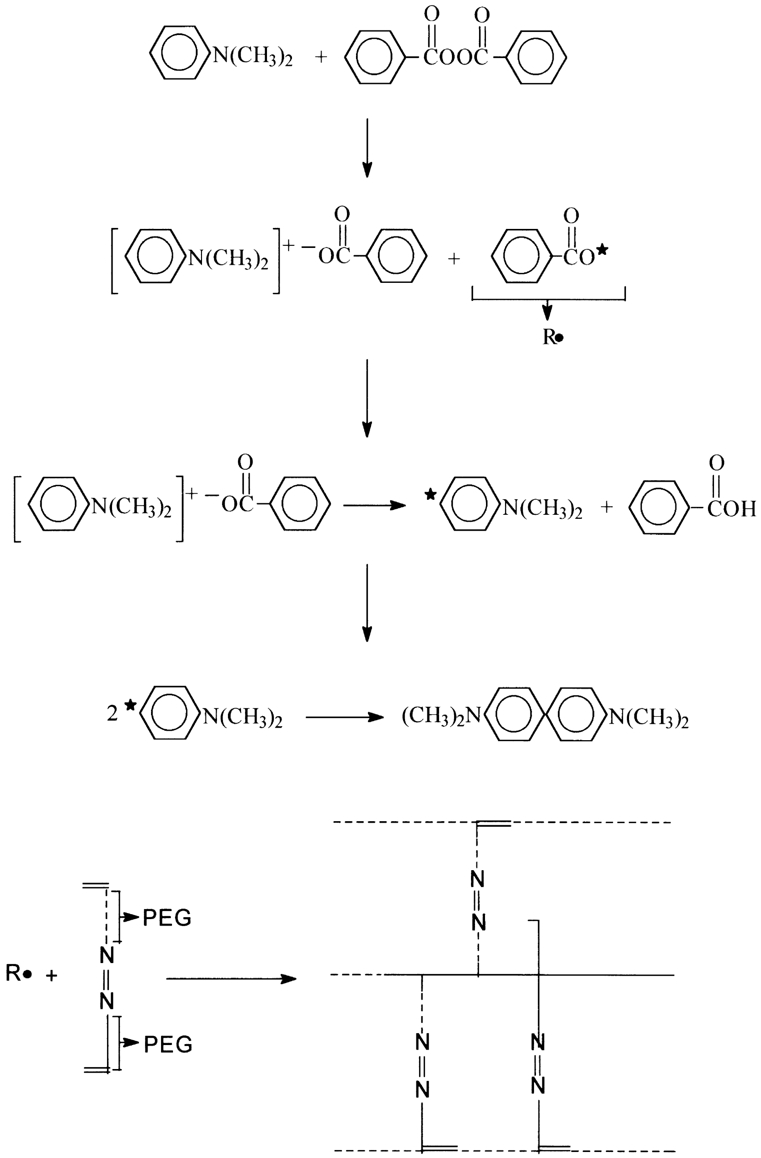
After the determination of swelling ratios, crosslinked polymers were polymerized again as follows: a small amount of crosslinked polymer (0.3 g) was placed in a hard glass tube and heated in nitrogen atmosphere at 100°C. After 3 h, the tube content was precipitated by pouring into methanol, filtered off and dried under vacuum at 25°C. Swelling ratios (q_v) and M_c values were calculated as q_v' and M_c'.

2.5. Determination of M_c values

The average molecular weight of the chain sections between crosslinks M_c, and the degree of crosslinking are important factors for the characterization of three

Table 1
Dispersion copolymerization of MMA with MIM-400 initiated by BPO/DMA redox system at 20°C

Run number	MIM-400 ($\times 10^2$ mol/l)	MMA (mol/l)	[BPO]:[DMA] (mol/mol)	q_v	M_c (g/mol)	q_v'	M_c' (g/mol)
1	1.98	2.59	1:1	21.9	112 560	17.2	73 250
2	4.36	2.51	1:1	18.2	81 420	12.1	38 200
3	6.03	2.46	1:1	17.4	75 470	9.5	23 980
4	9.77	2.33	1:1	16.8	70 610	9.0	21 490
5	13.38	2.21	1:1	16.1	64 660	8.7	20 160
6	1.95	2.56	5:1	14.2	51 700	12.5	40 470
7	4.32	2.49	5:1	9.3	22 930	8.9	21 070
8	5.97	2.43	5:1	8.1	17 400	7.7	15 760
9	9.68	2.35	5:1	7.0	12 970	6.4	10 810
10	13.26	2.19	5:1	6.5	11 120	6.0	9 430



Scheme 2.

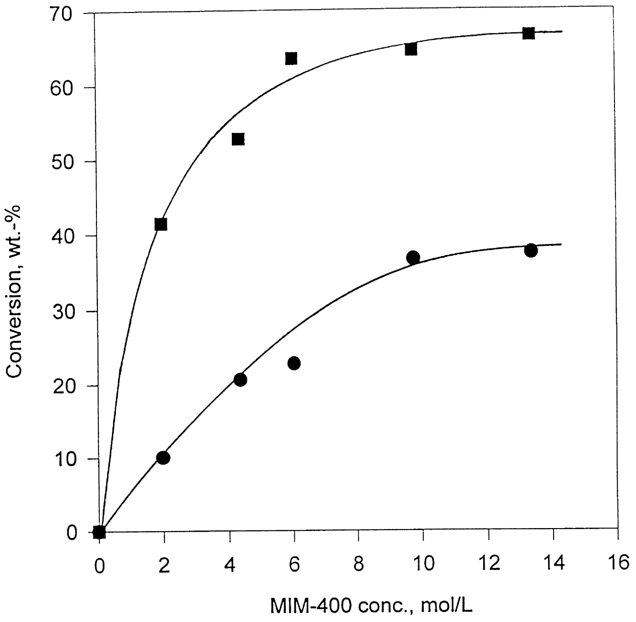


Fig. 1. Plot of conversion versus MIM-400 concentration. –●–, [BPO]/[DMA] = 1:1; –■–, [BPO]/[[DMA] = 5:1.

dimensional networks [15]. The quantity M_c can be evaluated from swelling measurements through application of the Flory–Rehner equation [16]:

$$\frac{1}{M_c} = -\frac{\ln(1 - v_2) + v_2 + x_{12}v_2^2}{\rho V_1(v_2^{1/3} - \frac{1}{2}v_2)}$$

where v_2 the reciprocal of the equilibrium volume swelling degree (q_v), V_1 the solvent molar volume, ρ the polymer density and χ_{12} the polymer–solvent interaction parameter.

χ_{12} was calculated from the Hildebrand and Scott solubility parameters δ_p and δ_s:

$$\chi_{12} = B + V_1/RT(\delta_p - \delta_s)^2$$

where δ_p and δ_s are solubility parameters of the polymer and swelling solvent, respectively, B the lattice constant, the value of which taken as 0.34 [17].

3. Results and discussion

We have chosen MIM-400 prepared from PEG-400, 4,4′-dicyano-4,4′azovaleryl chloride (ACPCL) and 4-vinylbenzyl chloride (VBCL), in order to study the macrocrosslinker property of macroazoinimers. Using redox initiator pair, MIM-400 was copolymerized with MMA at 20°C. Hence, only the macroazoinimer was used as a crosslinker. Results and conditions of the dispersion copolymerization are tabulated in Table 1. The reaction between BPO and DMA yields two types of free radicals; benzoyl and dimethylaniline radicals. The dimethylaniline radical does not initiate the polymerization [18,19]. This radical is stabilized by resonance, and the recombination of these radicals as suggested by the third step of the reaction given later would seem more likely to occur. Radical formation and the fate of radicals are illustrated in Scheme 2. The product of this step is a colored compound, and we observed that as the concentration of the DMA was increased, the color of the polymers obtained was darkened. The violet color of these samples was due to the adsorbed adduct products of the DMA radicals. When these colored polymer samples were dissolved in THF and reprecipitated by methanol, colorless polymer was obtained.

It is therefore clear that the benzoyl radicals produced during the first step of the reactions are the precursors of the polymerization reaction.

Dispersion copolymerization of MMA with MIM-400 initiated by the BPO/DMA pair gave PMMA-PEG networks containing undecomposed azo groups in the main chain as shown in Scheme 2. MMA was polymerized with a crosslinked polymer containing azo groups without any initiator in oil bath thermostated at 60°C for 3 h. Thus, undecomposed azo groups of polymer network were verified.

In order to evaluate the effect of the [BPO]:[DMA] ratio, the first set of experiments was designed at a fixed ratio [BPO]:[DMA] of 1:1, while the concentration of MIM-400 was changed in a range between 1.98 and 13.38 mol/l. The concentration of MMA was 2.50 mol/l. The second set of experiments was carried out at a fixed ratio [BPO]:[DMA] of 5:1. In each case, [DMA] was 2.3×10^{-2} mol/l.

For each run M_c values were determined according to Flory–Rehner equation (Table 1). The chain length between junction points, M_c, have been changed with MIM-400 concentration and [BPO]:[DMA] ratio. When MIM-400 concentration and [BPO]:[DMA] ratio increases, the M_c values of the network decreases. In higher amount of BPO, the produced radicals can polymerize most of the vinyl groups of MIM-400 and thus the polymer network becomes denser and the M_c values become lesser. In the case of 1:1 ratio, much less number of radicals are produced. The amount of radicals would not be enough to polymerize much vinyl groups of MIM-400. Therefore, the number of polymerized vinyl groups of MIM-400 gets relatively smaller than the ratio of 5:1. The greater M_c values indicates that the polymer network contains higher pending vinyl groups. To confirm this, the polymeric yields were heated in nitrogen atmosphere at 100°C for 3 h and q_v and M_c values were again calculated as q_v' and M_c'. These values are tabulated in Table 1, and it can be clearly seen that the decrease in the q_v and M_c values are higher in the network of 1:1 ratio than in 5:1. This verifies the idea of the existence of higher pending vinyl groups in the networks of 1:1 ratio.

We also can infer that the increase in the DMA concentration causes an increase in the M_c values of the networks. The explanation is that the increase in the DMA concentration further retards the crosslinking level which results in the decrease of the swelling and M_c.

Conversion-MIM-400 concentration plot is shown in Fig. 1. The effect of variations in MIM concentration and

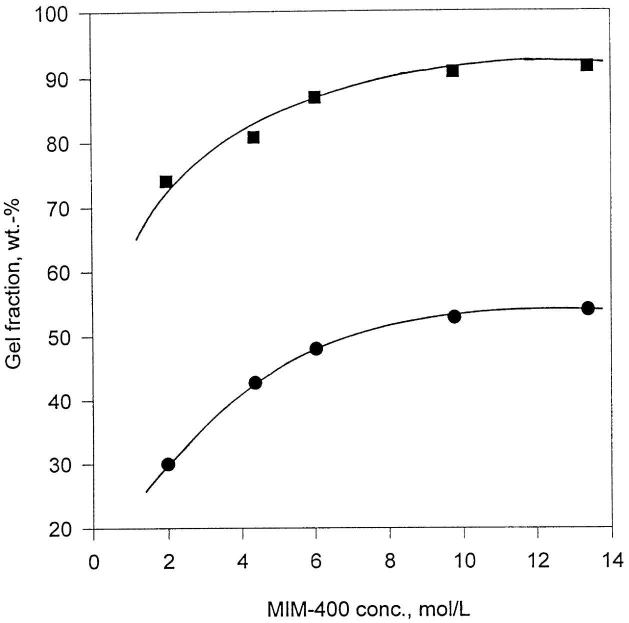


Fig. 2. Plot of gel fraction versus MIM-400 concentration. –●– [BPO]/[DMA] = 1:1; –■– [BPO]/[DMA] = 5:1.

[BPO]:[DMA] ratio on the percentage of conversion is given in this figure. The polymer yield steadily increased with the increasing MIM-400 concentration and [BPO]:[DMA] ratio. This result is similar to the one that was carried out by Imoto, Otsu and Ota (Ref. [4]).

Fig. 2 indicates the gel fractions of the polymer networks for the dispersion copolymerization of MMA that was initiated by the system BPO/DMA in the presence of MIM-400. The gel fractions were between 30.0 and 54.0 for the 1:1 ratio of [BPO] to [DMA] and between 74.1 and 91.6 for the second set (5:1). The gel fraction increased by two times at lower BPO concentrations.

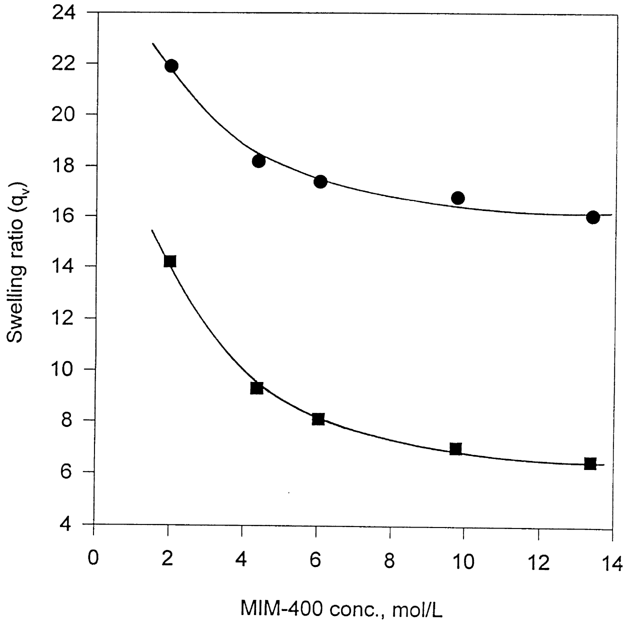


Fig. 3. Plot of swelling ratio versus MIM-400 concentration. –●– [BPO]/[DMA] = 1:1; –■– [BPO]/[DMA] = 5:1.

Fig. 3. indicates the swelling ratios, q_v, of the polymer networks. Swelling ratios were between 21.9 and 16.1 for the 1:1 ratio [BPO]:[DMA] and between 14.2 and 6.5 for the 5:1 ratio. The increasing MIM-400 concentration and [BPO]:[DMA] ratio, causes higher gel polymer fraction but lower swelling ratio of the gel polymer. This result was expected because the vinyl content of the macrocrosslinker increases as the concentration of MIM-400 increases.

Besides, dispersion polymerization of MIM-400 with MMA was carried out in a shaker thermostated at 60°C for 24 h. Polymerization was carried out according to the procedure cited in Ref. [11] while MIM-400 was used as a macrocrosslinker and as a macroinitiator. The amount of MMA, ethanol/water ratio and MIM-400 were kept constant as; 1.0 g, 4/1 (v/v) and 0.5 g, respectively. Gel fraction, q_v and M_c values were determined as; 90 wt.%, 5.86 and 8950 g/mol, respectively. In the present work, MIM-400 was used both as an initiator and as a crosslinker. q_v and M_c values were found much lesser when compared to run numbers 3 and 8 where equal amounts of MIM-400 was used, in Table 1. This result was much expected, as the gelation behavior of MIM was remarkably different from that of the macrocrosslinkers [10].

In conclusion, macroazoinimer as a macrocrosslinker lead to crosslinked block copolymers containing undecomposed azo groups. The dispersion copolymerization of MMA with MIM-400 can be carried out at lower temperatures using BPO/DMA redox pair. BPO and MIM concentrations are very effective on the crosslinking polymer yield and the crosslinking structures.

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References

[1] Nagarajan S, Kumari SSS, Srinivasan KSV. J Appl Polym Sci 1997;63:565.
[2] Çakmak İ. Makromol Rep 1995;A32:197.
[3] Saccubai S, Santappa M. J Polym Sci 1969;A1:643.
[4] Imoto M, Otsu T, Ota T. Angew Makromol Chem 1955;10.
[5] Meltzer TH, Tobolsky AV. J Am Chem Soc 1954;76:5178.
[6] O'Driscoll KF, Schmidt JF. J Polym Sci 1960;35:189.
[7] Hazer B. Macromol Rep 1991;A28:47.
[8] Hazer B. Makromol Chem 1992;193:1081.
[9] Hazer B, Erdem B, Lenz RW. J Polym Sci Part A: Polym Chem 1994;32:1739.
[10] Yıldız U, Hazer B. Macromol Chem Phys 1998;199:163.
[11] Yıldız U, Hazer B, Capek I. Angew Makromol Chem 1995;231:135.
[12] Nagash HJ, Okay O, Yildirim H. J Appl Polym Sci 1995;56:477.

[13] Okay O. Makromol Chem 1988;189:2201.
[14] Hamurcu E, Baysal BM. Polymer 1993;34:5163.
[15] Eroğlu MS, Güven O. Polymer 1998;39:1173.
[16] Widmaier JM, Sperling LH. Macromolecules 1995;15:625.
[17] Gupta GN, Srivastava AK. Macromolecules 1995;28:827.
[18] Samay G, Kubin M, Podesva J. Angew Makromol Chem 1978;72:185.
[19] Senel S, Yörüksoy BI, Güven O. Tr J Chem 1996;20:62.