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Bifunctional Initiators

3. Synthesis of Poly(Methylmethacrylate-b-Styrene) and Poly(Methylmethacrylate-b-Acrylonitrile) Block Copolymers

A. S. Shaikh, S. Dumitriu, Eugenia Comăniță and C. I. Simionescu

Department of Organic and Macromolecular Chemistry, Polytechnic Institute,
6600 Jassy, Romania

Dedicated to Prof. Charles Overberger at the occasion of his 60th anniversary

SUMMARY

Poly(methylmethacrylate-b-styrene) and poly(methylmethacrylate-b-acrylonitrile) block copolymers are synthesized by means of the 4,4'-azo-bis-(4-cynovaleryl)-benzoyldiperoxide.In the first stage a polymethylmethacrylate prepolymer is synthesized using the above mentioned initiator.The prepolymer containing peroxide end groups is employed in the second stage for the block copolymerization of styrene or acrylonitrile.The block copolymer structure was elucidated by means of IR and NMR spectral measurements.

INTRODUCTION

The bifunctional initiators are primarely used as initiators in radicalic polymerization as well as in block copolymer syntheses (SHEPPARD et al., 1978; SCHULZ and WEST, 1974). Vinylic polymers of high molecular weights (YERIGOVA and IVANCHEV, 1969) and improved properties were thus obtained. The block copolymers are easely accesible and can be controlled structurally by the amount of bifunctional initiator and synthesis conditions.

In the present paper the syntheses of same block copolymers using 4,4'-azo-bis-(4-cynovaleryl)-benzoyldiperoxide (SIMIONESCU et al., 1980) as initiator are reported.

RESULTS AND DISCUSSION

Due to the sequential fragmentation the azoperoxidic initiators are suitable for obtaining macromolecular chains containing peroxidic end groups which are able to initiate subsequently a new polymerization process resulting in a block copolymer formation.

In the present paper a prepolymer of polymethylmethacrylate (PMMA) with peroxidic end groups was obtained in the first stage.The bulk polymerization was carried out at different temperatures and initiator concentra-

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tions which resulted in variations in the yield, viscosity and molecular weight of the polymer (Table 1).

TABLE 1
Variation of the yield, intrinsic viscosity and molecular weight of PMMA with temperature and initiator concentration

Initiator concentration (%)	Yield (%)	$[\eta]$ (dl/g)	$M_v \cdot 10^{-5}$ ± 10%	$M_w \cdot 10^{-5}$ ± 10%	$M_n \cdot 10^{-5}$ ± 10%
		Temperature = 80°C, Time = 60 min			
2	82.60	0.56	1.75	1.86	1.24
1	82.00	0.62	2.00	3.60	1.80
0.50	80.00	0.96	3.66	6.44	3.24
0.25	68.00	1.06	4.18	7.70	3.85
		Temperature = 70°C, Time = 60 min			
2	81.00	-	-	1.95	0.98
1	76.00	0.85	3.09	6.99	3.01
0.50	30.00	0.98	3.76	8.16	3.26
0.25	16.00	1.14	4.62	7.98	3.27
		Temperature = 60°C, Time = 60 min			
2	22.4	0.82	2.95	3.95	2.63
1	15.6	1.01	3.91	7.08	3.52
0.50	11.8	1.07	4.24	6.17	3.98
0.25	4.4	-	-	-	-

$$M_v = \left[\frac{[\eta]}{K} 100 \right]^{1/a} \quad K \cdot 10^3 = 8.35 \quad a = 0.73$$

The reaction product contains both active macromolecular chains with peroxide end groups and inactive chains. Their ratio depends on the time, temperature and initiator concentration. The active chain content decreases with increasing time and temperature, namely from 31.6% (t = 60°C, time = 60 min) to 11.3% (t = 80°C, time = 60 min). Since with MMA polymerization the interruption stage proceeds primarely by disproportionation reactions (BEVINGTON and MELVILLE, 1954) the macromolecules will contain a single peroxide end group. A kinetical study was carried out on the methylmethacrylate polymerization in o-dichlorobenzene solution with 4,4'-azo-bis-(4-cyanovalery)-benzoyldiperoxide as initiator in order to determine the reaction rate and order. The experiments were carried out under nitrogen atmosphere, at 74°C, with monomer concentration of 2.0856, 1.368 and 0.648 mol/l and 1% initiator concentration towards the monomer. The conversion was followed gas-chromatographically by using a 5% polyethylen-

glycol adipate column of 0.7 m on chromosorb P, at 160°C and argon stream of 18 l/min.
From the conversion - time plot (Figure 1) the polymerization rates for the three concentrations were calculated: $v_1 = 20.276.10^{-5}$ mol/l.s, $v_2 = 7.2.10^{-5}$ mol/l.s, $v_3 = 2.195.10^{-5}$ mol/l.s. From the lnv - lnC plot the reaction order of 2 and reaction rate constant of $6.46.10^{-6}$ $l.mol^{-1}.s^{-1}$ were found.

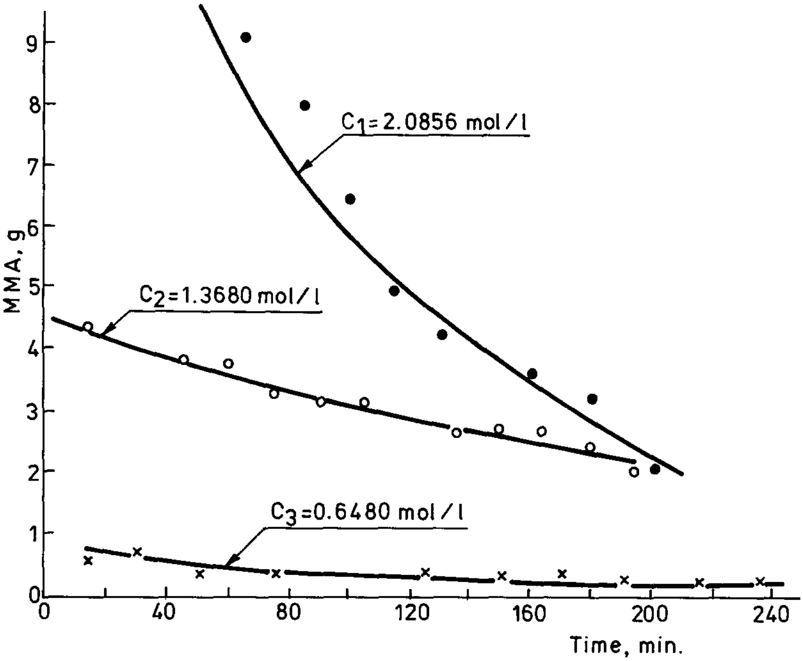
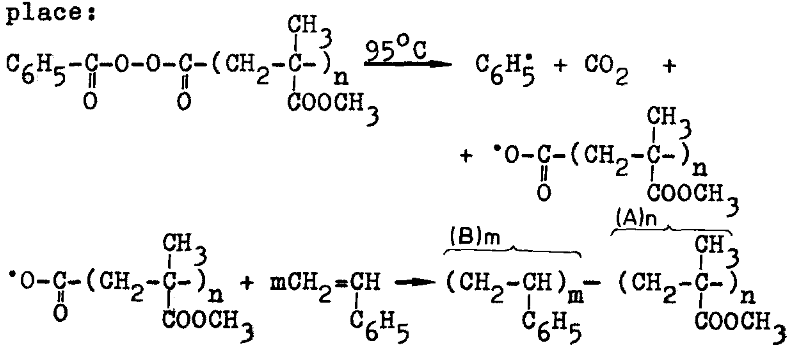


Fig. 1. The conversion - time plot

The block copolymerization was carried out adding styrene to a benzene solution of the purified prepolimer, at an weight ratio of 7/1.The reaction mixture was heated at 95°C for 7 hours.The following reactions take place:



$$C_6H_5-\underset{\overset{\|}{O}}{C}-O-O-\underset{\overset{\|}{O}}{C}-(CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-)_n \xrightarrow{95^oC} C_6H_5^{\bullet} + CO_2 + {}^{\bullet}O-\underset{\overset{\|}{O}}{C}-(CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-)_n$$

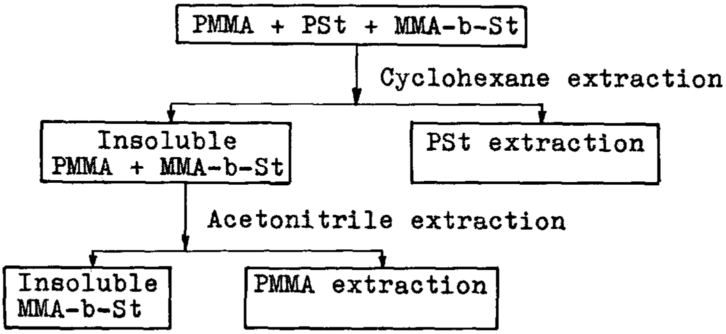
$${}^{\bullet}O-\underset{\overset{\|}{O}}{C}-(CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-)_n + mCH_2{=}\underset{C_6H_5}{CH} \longrightarrow \overbrace{(CH_2-\underset{C_6H_5}{CH})_m}^{(B)m}-\overbrace{(CH_2-\overset{CH_3}{\underset{COOCH_3}{C}}-)_n}^{(A)n}$$

A certain amount of homopolymer (polystyrene) is also formed beside a small amount of unconverted polymethylmethacrylate.
The interruption of the polystyrene chaine increase may result in formation of several structures.

$$2\cdot(B)_m-(A)_n \xrightarrow{\text{recombination}} (A)_n-(B)_{2m}-(A)_n$$

$$2\cdot(B)_m-(A)_n \xrightarrow{\text{disproportionation}} 2(B)_m-(A)_n$$

The mixture of block copolymers and homopolymers was separated according to the following scheme (PIIRMA and CHOU, 1979):



In table 2 the composition of the block copolymer purified as described above is given.

TABLE 2
Separation results

wt % PSt	wt % PMMA	wt % Block	Styrene molar content in block (%)
4	14	82	21.3[a] 80[b]

a- Before separation of homopolymers (from fig.2)
b- After separation of homopolymers (from fig.3)

The block copolymer structure was elucidated by means of IR and NMR spectral measurements (figure 2,3).
The IR spectrum of poly(methyl methacrylate -b- styrene) show the absorption bands characteristic of polystyrene at 690, 920, 810, 2940, 3040 cm^{-1} and of polymethyl methacrylate at 1750 cm^{-1}.
The NMR spectrum (figure 3) shows signals at the following δ values: 0.95, 1.05 (CH_3); 1.85 (CH_2); 6.5, 6.95 (C_6H_5) ppm.
The poly(methylmethacrylate-b-acrylonitrile) block copolymer was prepared similarly starting from the

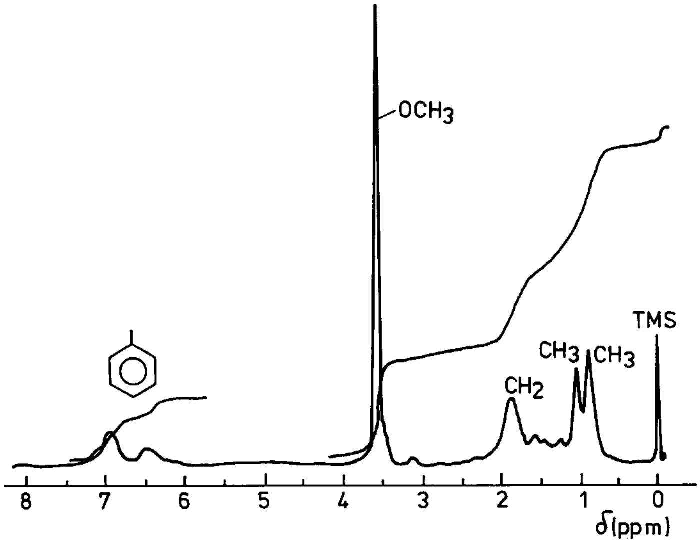


Fig. 2. The NMR spectrum of block copolymer containing both homopolymers.

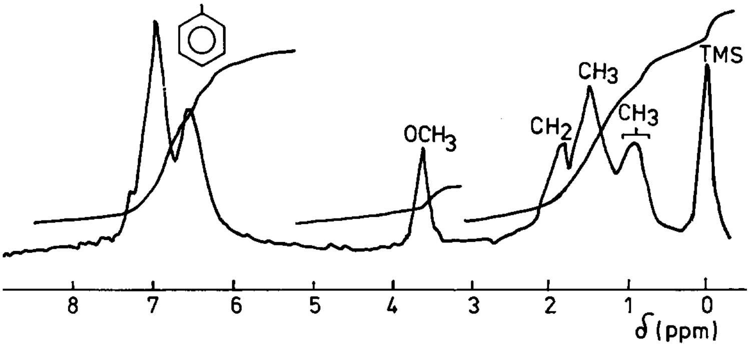


Fig. 3. NMR spectrum of the block copolymer after removing of the homopolymers.

same prepolymer. In this case a mixture of block copolymer and homopolyacrylonitrile is separated from the benzene solution. The block copolymer was purified by succesive extractions in acetone and dimethylformamide. By extracting then the resulted product in the same solvents its nitrogen content remains constant.
The IR spectrum of the block copolymer shows absorption bands characteristic of polyacrylonitrile (2240 cm^{-1} νCN) and polymethylmethacrylate (1740 cm^{-1} νCO).

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