Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

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To cite this Article Nair, C. P. Reghunadhan , Chaumont, P. and Clouet, G.(1990) 'A-B-A Triblock and (A-B)$_n$ Segmented Block Copolymers of Styrene and Ethylene Oxide via Thermal Iniferters', Journal of Macromolecular Science, Part A, 27: 6, 791 — 806

To link to this Article: DOI: 10.1080/00222339009349658

URL: http://dx.doi.org/10.1080/00222339009349658

J. MACROMOL. SCI.—CHEM., A27(6), pp. 791–806 (1990)

A-B-A TRIBLOCK AND $(A\text{-}B)_n$ SEGMENTED BLOCK COPOLYMERS OF STYRENE AND ETHYLENE OXIDE VIA THERMAL INIFERTERS

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ABSTRACT

A free radical technique is described for the synthesis of tri- and multiblock copolymers of styrene and ethylene oxide through polyethylene oxide-based thermal "iniferters." The mono- or dihydroxy-terminated oligomeric polyethylene oxides were chemically transformed to the secondary amine terminated species. Thiocarbamylation and oxidation of the amine groups gave rise to macro- or polymeric thiuram disulfides called macro- or polymeric "iniferters," respectively. Thermal polymerization of styrene in the presence of the macro iniferter led to the formation of their perfect triblock copolymers, with styrene forming the central block. Utilization of the polymeric iniferter, on the other hand, give rise to $(A\text{-}B)_n$ type segmented copolymers containing as many as 3 (A-B) sequences. The length of each block could be regulated by the choice of the appropriate iniferter and its relative concentration with respect to the monomer. The iniferters and the block copolymers were characterized.

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INTRODUCTION

Block copolymers containing separate hydrophobic and hydrophilic segments find potential application as stabilizers of aqueous dispersions because of their amphiphilic nature. They can act as effective polymeric surface-active materials in aqueous emulsion polymerization. Their action would be expected to be dependent on the length and distribution of each sequence in the polymer. The block copolymers of styrene and ethylene oxide are typical examples of this class of compounds owing to the extreme differences in the solubility characteristics of the two blocks.

Their syntheses are normally performed by anionic initiation. Heitz described a free radical technique for the synthesis of $(A\text{-}B)_n$ block copolymers of polyoxyethylene (POE) and polystyrene (PS) using polyethylene oxide-incorporating azo groups as the polymeric initiator [1]. But the polymeric initiator contains only short-chain POE. Chain end condensation has also been applied in some cases to synthesis diblock copolymers [2]. We have recently introduced the iniferter technique to the synthesis of tri- and multiblock copolymers of the addition-condensation [3, 4] or addition-addition [5] type. This free radical method makes use of the *ini*tiator, chain trans*fer*, *ter*minator (iniferter) property of thiuram disulfide groups incorporated into macromolecular chains. In this paper we illustrate the applicability of the technique to the synthesis of a typical amphophilic block copolymer, i.e., poly(styrene-*b*-ethylene oxide). The method is base on the use of macro- and polymeric thiuram disulfide of PEO as initiator for styrene polymerization. The paper describes the syntheses and characterization of the iniferters and the block copolymers resulting from them.

EXPERIMENTAL

Materials

Styrene was purified by vacuum distillation from finely powered CaH_2. Thionyl chloride, pyridine, and toluene were purified by distillation. CS_2, I_2, and triethylamine (Aldrich) were used as received. The hydroxyl-terminated polyoxyethylene (POE) was procured from Aldrich.

Instruments

NMR was recorded on a Brucker 60 MHz spectrometer. DSC analyses were performed on a Perkin-Elmer thermal analyzer coupled with a thermal analysis data station. Molecular weights were determined by GPC analysis using THF as eluent and a refractive index detector. Polystyrene and polyoxyethylene standards were used for calibration. Viscosities were determined with a capillary-type viscometer.

Synthesis of Secondary Amine-Terminated PEO

In a typical experiment, 25 g dihydroxy POE (MW 3400) was dissolved in 150 mL toluene and dried by azeotropic distillation by recovering about 30 mL toluene. To the system after cooling to room temperature were added pyridine (0.05 mol) followed by thionyl chloride (0.05 mol), drop by drop. The system was stirred for 4 h. The pyridine hydrochloride was filtered off and the residue was precipitated in ether to recuperate the dichloro-POE which was dried in vacuum. Yield: quantitative.

To 20 g of the above dichloro compound dissolved in 20 mL dry acetonitrile was added piperazine (5 g, 0.06 mol). The mixture was heated to 85°C and kept reacting at that temperature for 8 h. The solution was cooled, diluted with 100 mL toluene, filtered, and the polymer was further purified by reprecipitation in ether from toluene solution.

Synthesis of Iniferters

The above amine-terminated PEO (20 g) was dissolved in 100 mL toluene. Triethylamine (1 mL) and CS_2 (1 mL) were added, followed by a solution of I_2 in toluene until the end point was reached. The solution was filtered and the poly(thiuram disulfide) was precipitated in ether. It was dried in vacuum at room temperature, characterized by elemental analysis, and the molecular weights determined by viscometry or GPC.

The other iniferters were synthesized under exactly the same conditions. The characterizations were done by elemental and GPC analyses.

Block Copolymer Synthesis

The polymerizations were performed in sealed evacuated ampules. The ampules containing styrene, iniferter, and solvent (toluene) were sealed after the usual freezing, thawing, and evacuating. The polymerization was done at 85°C in electrically controlled oil baths. After polymerization, the contents, diluted with tetrahydrofuran, were precipitated directly into methanol for low POE-loaded systems. For the others, the precipi-

TABLE 1. Characteristics of the Iniferters and Their Elemental Analyses

Nature of the prepolymer	Molecular weight of prepolymer	Molecular weight of iniferter	Elemental analysis of the iniferter[a] C, % Calc	C, % Found	H, % Calc	H, % Found
POE-OH	2,000	5,500[b]	53.22	53.29	8.80	8.89
POE-OH	5,000	14,000[b]	53.59	53.06	8.90	8.90
HO-POE-OH	3,400	17,600[c]	53.16	52.37	8.77	8.67

[a] Calculated for complete functionalization. For PI calculation based on the observed molecular weight.

[b] $\bar{M}_p$ in GPC, deemed as equal to $\bar{M}_n$ of the fraction eluted at this point.

[c] Calculated from $[\eta]$.

tation was first done in heptane. The precipitates were collected by filtration and were extracted 3 or 4 times with methanol to remove the unreacted POE. The polymers were recovered by filtration, washed with methanol, and dried.

The molecular weights were determined by GPC analyses and the composition by elemental analysis.

RESULTS AND DISCUSSIONS

In earlier studies it had been well illustrated that the use of polymeric iniferters in vinyl polymerization gives rise to multiblock copolymers, while the macro iniferter (containing only one thiuram disulfide group)

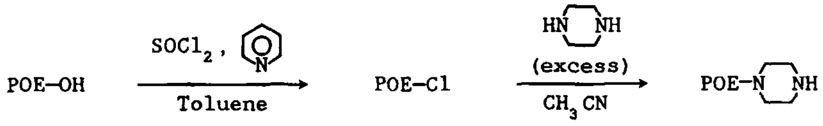
TABLE 1. Continued

Elemental analysis of the iniferter[a]					
N, %		S, %			
Calc	Found	Calc	Found	Comments	Ref. of the iniferter
1.36	1.20	3.10	1.66	Iniferter is only 53% pure. The remainder is functional and amine-coupled polymer	MI-2000
0.54	0.67	1.24	1.13	% Purity: 91%	MI-5000
1.21	1.46	2.76	2.78	The polymeric iniferter contains an average of 4.8 POE units	PI

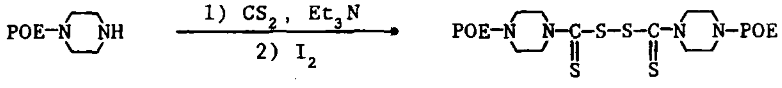
yields triblock copolymers. In this work for the synthesis of copolymers of ethylene oxide with styrene, we used iniferters based on POE as the thermal initiator for styrene.

Synthesis and Characterization of Iniferters

For this synthesis, the hydroxyl groups on POE were first transformed to chloro groups. Their reaction with excess piperazine fixed the secondary amine groups at the chain ends. They were then transformed into the thiuram disulfides by reaction with CS_2 and iodine. The overall reaction scheme is depicted as

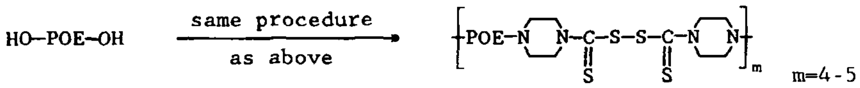


1)



Macroiniferter (MI)

2)



Polyiniferter (PI)

The macro- and the polymeric iniferters were characterized by elemental analysis. Their molecular weights were determined earlier by GPC analysis or by viscometry. In this study, two types of MIs were synthesized using OH-terminated POE of molecular weights 2000 and 5000. For the PI a dihydroxy-terminated POE having a molecular weight of 3400 was used. Analysis of the chloro compounds showed that chlorination was quantitative. The intermediate amines were not characterized directly but were characterized indirectly in terms of their thiuram disulfides. The thiocarbamylation is a clean reaction. The characteristics of the iniferters are shown in Table 1. Their elemental analysis showed that the amination reaction was not quantitative. This left some nonfunctional POE in the macro-iniferters which did not interfere in the subsequent reaction. Their amount, as calculated from elemental analysis (%S), is given in Table 1. The MIs, when examined by GPC, showed that the molecular weights had clearly doubled. For comparison, the peak mass (M_p) in GPC of the iniferters and their precursors were used. The GPC analysis of the amine also indicated that piperazine causes some coupling between the POE chains. However, their amount was not considerable for the high molecular weight POEs. The discrepancy in the ratio of N and S content in some cases is due to this side reaction. The GPC traces of a MI and its precursors can be seen in Fig. 1. The unreacted POE can be seen as a separate peak in the GPC of the MI. The molecular weight of the PI as deter-

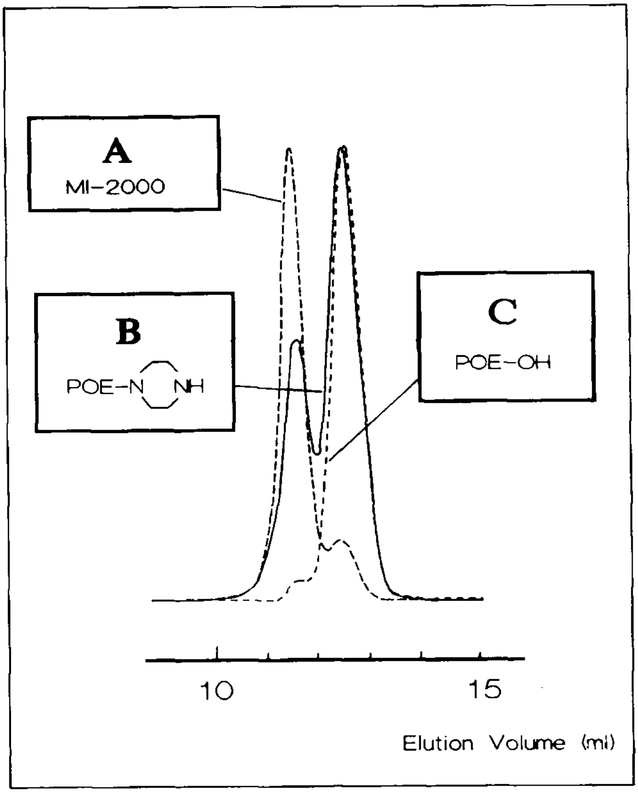


FIG. 1. GPA traces of: A, macro-iniferter MI-2000; B, its amine precursor; and C, its OH precursor.

mined from its [η] showed a degree of chain extension of about 4. The elemental analysis of the PI, shown in Table 1 along with those of the MIs, was quite consistent with the degree of chain extension observed.

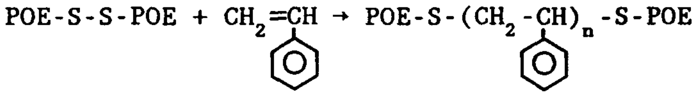
POE-PST-POE Triblock Copolymer

Using the macro-inferters MI-2000 and MI-5000 for the thermal polymerization of styrene, the triblock copolymers having two different POE sequence lengths could be prepared. The reaction scheme is

TABLE 2. Synthetic Conditions and Characteristics of the Triblocks Copolymers

Macroiniferter	Concentration of MI (g/dL) of monomer	Yield, %	Volume of toluene	Effective $[M]/[MI]^{1/2}$
MI-2000	5	55	0	109.5
	10	50	0	77.5
	15	55	0	63.3
	20	57	0	54.7
MI-5000	10	45	0	92.6
	16.7	48	0	71.7
	23.3	48	0	60.6
	30	63	0	53.5
	50	22	100	29.3
	70	22	100	24.7

[a] Calculated based on $\bar{M}_p$ of the iniferter in GPC.



$$\text{POE-S-S-POE} + CH_2{=}\underset{C_6H_5}{CH} \rightarrow \text{POE-S-}(CH_2\text{-}\underset{C_6H_5}{CH})_n\text{-S-POE}$$

The block copolymer is formed thanks to the triple function of the thiuram disulfide groups. The mechanism of polymerization can be envisaged as a simple insertion of the polystyryl block across the disulfide linkage. The length of the styryl block is a function of the iniferter concentration in the system. As in any free radical polymerization, the vinyl block length decreases systematically as the iniferter concentration increases. The copolymers having different PS block lengths could thus be synthesized using different concentrations of the two MIs. The synthetic details for the copolymers and their characteristics are given in

TABLE 2. Continued

$\bar{M}_n$ of copolymer (GPC) × 10^{-4}	I	% POE Calc[a]	% POE Found	Vinyl block length × 10^{-4}
8.80	2.2	5.3	8.3	8.34
4.30	2.6	9.3	10.0	3.90
3.40	2.3	13.5	13.6	2.94
2.86	2.6	16.1	16.7	2.40
8.5	1.9	16.5	13.5	7.1
7.2	1.8	19.4	18.7	5.8
6.5	1.8	21.5	21.6	5.1
5.7	2.0	24.6	29.0	4.3
4.1	1.5	34.2	36.5	2.7
3.9	1.5	35.9	36.6	2.5

Table 2. From the overall composition and the molecular weights, their structures were established as perfect triblocks. The variation of the vinyl blocks as a function of the iniferter concentrations are shown in Fig. 2. Since the vinyl block length should effectively be a function of the ratio $[M]/[MI]^{1/2}$, it has been plotted as a function of this ratio. It can be seen that vinyl block length is not only a function of the iniferter concentration but is quite dependent on the MI molecular weight for the cases studied. Increasing the molecular weight of the iniferter causes an increase in vinyl sequence length for the same effective $[M]/[MI]^{1/2}$ ratio. This shows that the initiating and terminating properties of the thiuram disulfide functions are subject to the translational restriction of the chain on which they are located. The triblock copolymers prepared even at about 60% conversion had excellent molecular weight distribution. The GPC traces of a few cases can be found in Fig. 3.

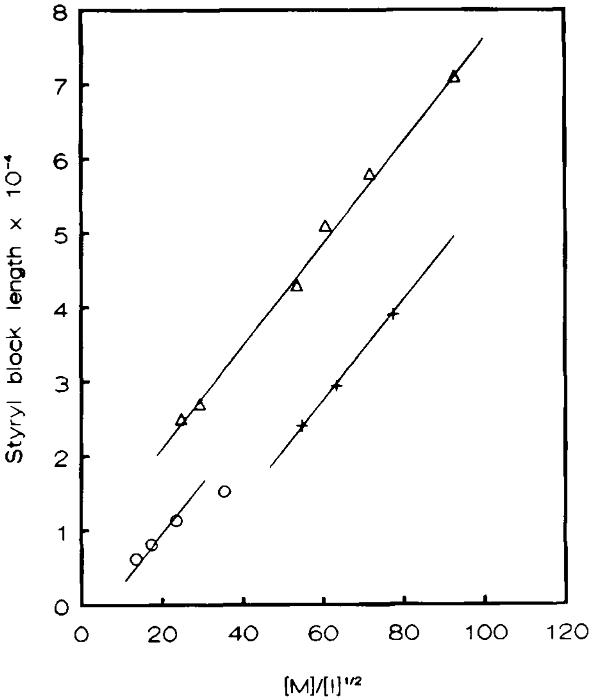


FIG. 2. Variation of polystyrene block length with the concentration of the iniferter for different cases: (×) MI-2000, (○) MI-5000, (△) PI.

Synthesis of POE-PS Multiblock Copolymers

The segmented block copolymers were synthesized by using the polymeric iniferter having a POE sequence length of 3400 and possessing an average of four polymer units per chain. The reaction scheme for their formation can be represented as

In this case the chain growth can be expected to take place by the simultaneous growth of styryl blocks between the various S—S linkages. The copolymers were prepared either by varying the iniferter concentration for maximum monomer conversion or by controlling the monomer conversion at a fixed PI concentration.

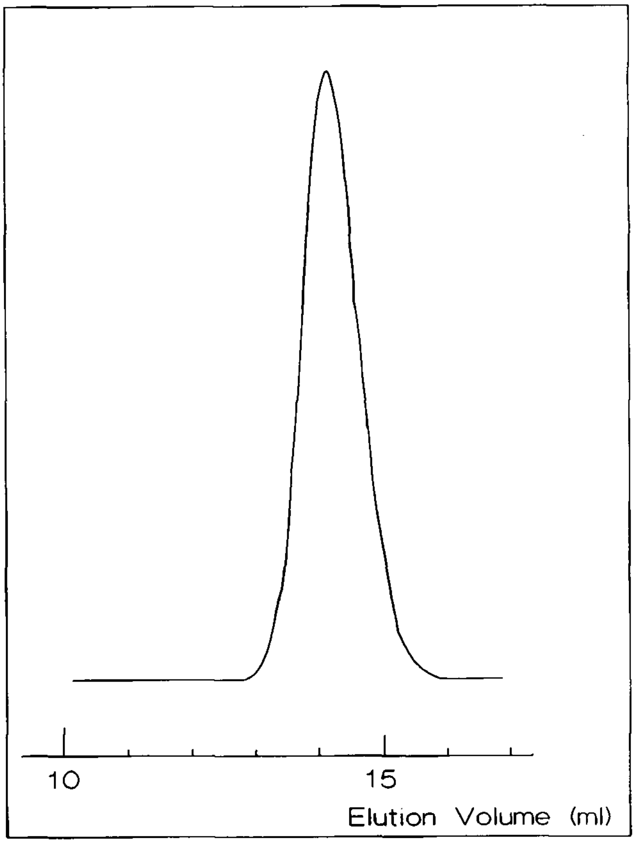


FIG. 3. GPC of a triblock copolymer using MI-5000, POE = 36%.

Varying the Monomer Conversion Technique

Table 3 presents the conditions for block copolymer synthesis. It can be seen that the molecular weight of the polymers increase with increasing monomer conversion which is consistent with the postulated mechanism of copolymer chain growth. At the maximum conversion it can be assumed that the polymer contains no active disulfide groups (longer time of polymerization). At this point of conversion, calculations show that the copolymer consists of as many as six alternating blocks. It can also be seen that a good fraction of the PI is consumed in copolymeriza-

TABLE 3. Characteristics of the Copolymers Synthesized at Varying Monomer Conversions

Polymerization conditions	Time, h	% Monomer conversion	$\bar{M}_n \times 10^{-4}$	I	% Iniferter consumed	Average number of PEA blocks at maximum conversion
[PI] = 10 mol/L vs monomer. Solvent: Toluene 100% by volume	7.5	21	4.2	2.4	66.6	4.4
	30	28	3.4	3.0	75.0	
	50	42.6	3.9	3.4	88.6	
	100	48	5.0	3.1	88.8	
[PI] = 15 mol/L vs styrene. Solvent: Toluene 100% by volume	7.5	17	3.1	2.6	37.8	6.3
	30	36	3.7	2.9	31.8	
	100	50	4.9	2.4	25.4	

TABLE 4. Synthetic Conditions and Characteristics of Copolymer at Maximum Monomer Conversion (time of polymerization: 72 h at 85°C) Using PI

Concentration of PI (g/dL) of monomer	Volume % of toluene	% Monomer conversion	$\bar{M}_n \times 10^{-4}$ of copolymer (GPC)	I
11.5	150	39	4.02	2.4
20	225	33	3.54	2.0
30	300	23	3.23	2.1
40	400	17	3.02	2.1

tion. Since the copolymers prepared at low monomer conversions may contain active disulfide groups, no attempts were made to establish their block structure. However, the study gives an overall insight into the evolution of the copolymer structure with conversion. The average number of blocks increases with an increase in monomer conversion.

Copolymer Synthesis at Maximum Monomer Conversion

The copolymers were synthesized by using two different concentrations of the PIs. In high PI loaded systems, toluene was added to decrease the viscosity. The polymerizations were allowed to proceed for 3 days to ensure complete thermal destruction of all disulfide groups. As seen in Table 4, the polymer yield is not considerable. This is due to the fact that the system is considerably diluted to render it less viscous especially at high PI loading (thereby reducing the rate of polymerization). Copolymers with different vinyl block lengths are formed, and the vinyl block length decreases with increasing PI concentration. Naturally, the POE content increases with an increase in PI concentration. The variation of the vinyl block length can be found in Fig. 2 which shows a behavior similar to that of macro iniferters. That is, the vinyl block length decreases with an increase in PI concentration in the system. The drastic decrease in vinyl length in this case for the same effective concentration of the iniferter is only a consequence of the immense dilution of the system. In radical polymerizations, the molecular weight of the poly-

TABLE 4. Continued

% POE found by analysis	Average number of alternating blocks *in the copolymer*	% Iniferter consumed at this monomer conversion	Average length of the styryl sequence
25.2	5.0	76.7	15 200
32.5	5.8	50.0	11 350
40.4	6.6	28.3	8 140
43.1	6.6	16.2	6 170

mer is directly proportional to the concentration of the monomer or, more precisely, to the ratio $[M]/[MI]^{1/2}$. Copolymers containing as many as six alternating blocks are formed. As the PI concentration increases, the number of A-B segments has a slight tendency to increase. In all cases, some unreacted PI was recovered, the percentage of which increases dramatically with increasing PI concentration and dilution. From these results it can be readily seen that the method cannot be applied to prepare POE-rich copolymers without risking the yield and the length of the styryl block.

Physical Properties of the Block Copolymers

The copolymers are in every example finely divided powders. They exhibit solubility characteristics similar to polystyrene. Even the copolymers containing 45% POE did not show the tendency to swell in water. Higher POE-containing copolymers were not prepared since the reaction system becomes increasingly viscous. DSC analysis showed that the POE blocks were immiscible with the polystyryl blocks in all cases; the POE blocks underwent independent transitions unaffected by PS. A representative DSC thermogram for a copolymer containing 40% POE is shown in Fig. 4 (multiblock copolymer, POE chain length 3400, molecular weight 30 200). The glass transition of POE can be seen at −60°C. Other thermal events, such as crystallization (−43°C) and fusion (36°C), can be seen along with the T_g of PS at 100°C.

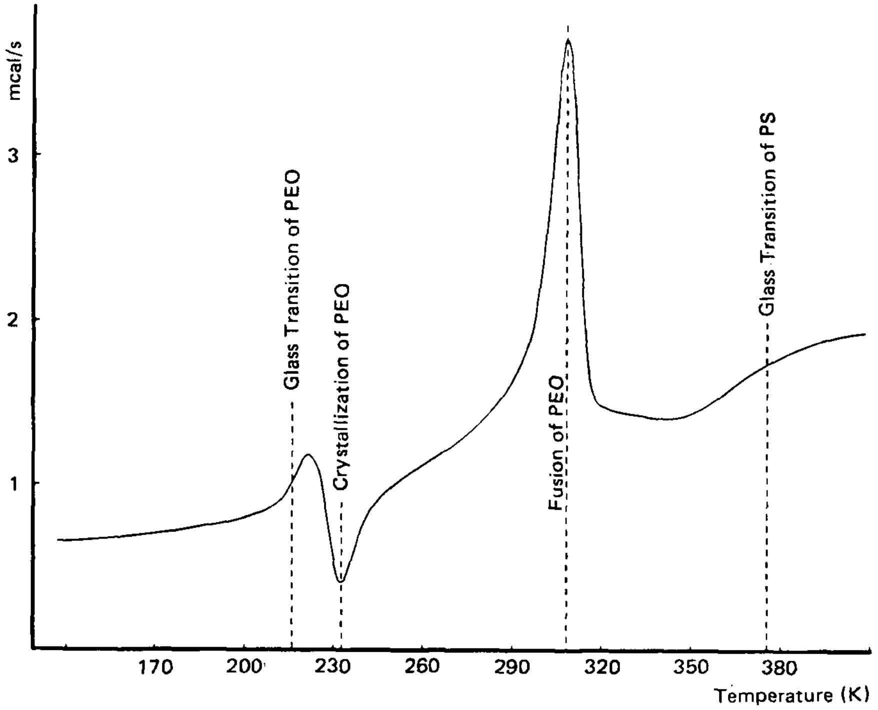


FIG. 4. DSC thermogram for a multiblock copolymer containing 40% POE. POE chain length = 3400, molecular weight = 30 200. Heating rate: 20°C/min.

CONCLUSION

The thermal iniferter technique for the synthesis of A-B-A and $(A\text{-}B)_n$ type block copolymers of POE and PS has been demonstrated. The copolymer characteristics can be controlled by choosing the appropriate iniferter and their concentration in the reaction system. The method is recommended for low POE content polymers.

ACKNOWLEDGMENT

Thanks are due to Mr. M. Keyser for doing the elemental analysis.

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Received September 27, 1989
Revision received November 29, 1989