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"LIVING" RADICAL POLYMERIZATION OF STYRENE USING DIPHENYLMETHANE DIISOCYANATE-BASED POLYURETHANE INIFERTER

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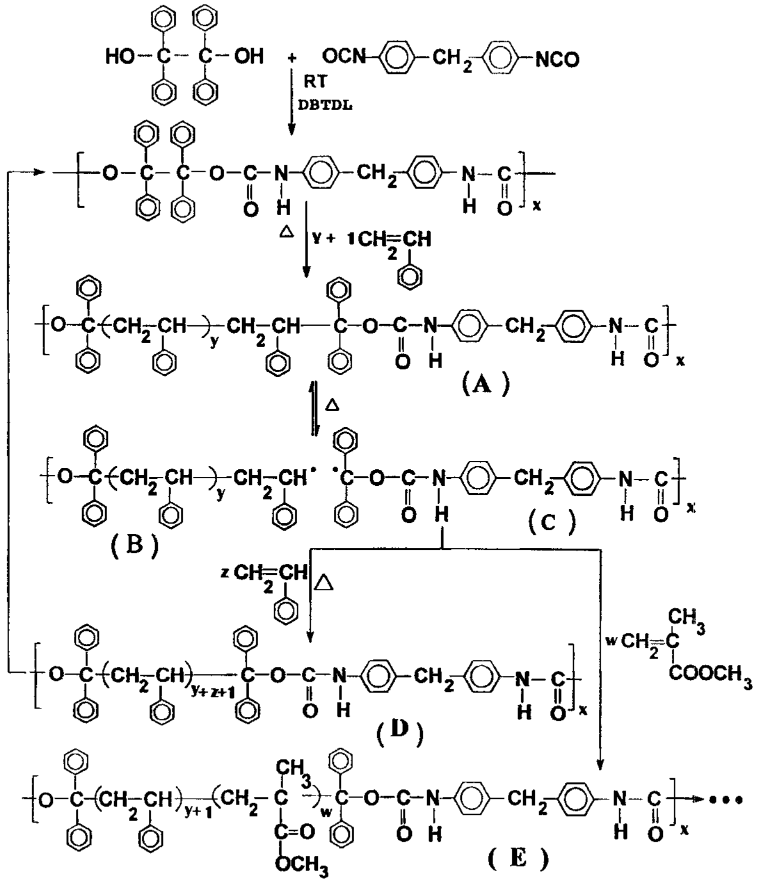
ABSTRACT

Polyurethane iniferter, synthesized from diphenylmethane diisocyanate and 1,1,2,2-tetraphenyl-1,2-ethanediol, was used to polymerize styrene. The increase of number-average molecular weight of the polystyrene while increasing both conversion and polymerization time prove that the polymerization of styrene using polyurethane iniferter is through a "living" radical mechanism. Postpolymerization of polystyrene in the presence of styrene and methyl methacrylate yielded high molecular weight polystyrene and polystyrene–polymethyl methacrylate block copolymers respectively.

INTRODUCTION

The chemoselectivity of radical polymerization can be improved by achieving reversible deactivation of the growing radicals. Reversible cleavage of covalent species, reversible formation of persistent radicals, and degenerative group transfer are the three possibilities to deactivate growing free radicals [1]. When the growing radicals are reversibly deactivated, the polymers/oligomers obtained are able to generate radicals at any time on supplying thermal or photo energy. As in the case of living ionic polymerizations where ions are always alive, here also radicals can be considered as always alive. Hence, if the growing radicals are reversibly deactivated, then the system is called a living radical polymerization. But all the growing radi-



SCHEME 1.

cals cannot be reversibly deactivated in radical polymerization. If the system consists of the meager presence of irreversible reactions, then the system is called a "living" radical polymerization [1]. Here quotation marks denote the meager presence of irreversible reactions.

Iniferters [2] (*ini*tiators, trans*fer* agents, and/or *ter*minators) are the best examples for the reversible deactivation of covalent species. Tetraphenylethane derivatives [2-4], thiuram disulfides [2, 5-9], and dithiocarbamates [5, 10, 11] are major iniferters which follow "living" radical polymerization. The "aged" chromium(II) acetate-benzoyl peroxide system [12, 13] and the triisobutylaluminum-2,2′-bipyridyl-2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) system [14, 15] fall in the reversible formation of the persistent radicals case. Radical polymerizations using alkyl halides [16-19] are examples of the degenerative transfer case. Recently, reversible deactivation of growing polymer radicals using TEMPO has been studied in detail [20-23].

Tetraphenylethane derivatives generate free radicals through homolytic cleavage of their central ethane bond [24, 25]. 1,1,2,2-Tetraphenyl-1,2-ethanediol (TPED) is a well-known free-radical initiator [26], but it neither serves as an inifer-

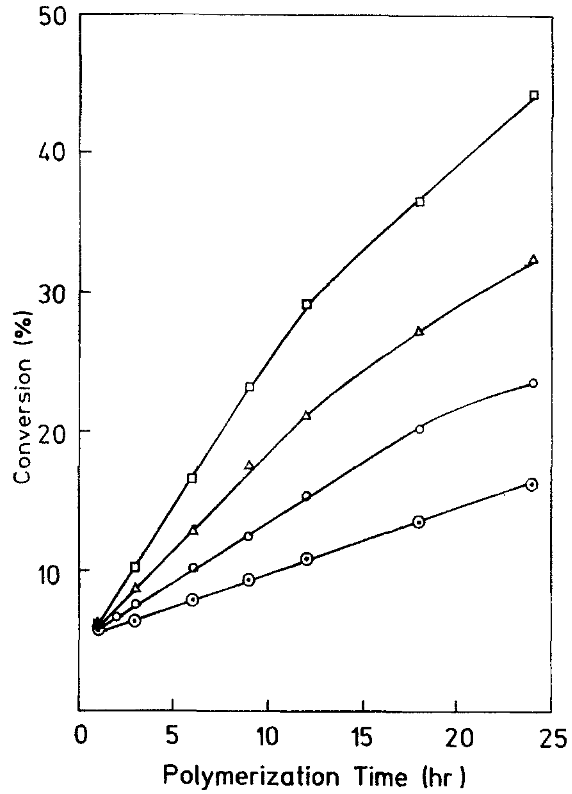


FIG. 1. Time-conversion plots for ST polymerization with PIM at various temperatures. (⊙) 65°C; (○) 70°C; (△) 75°C; (□) 80°C. $[ST]_0$ = 2.0 mol/L; $[PIM]_0$ = 0.02 mol/L.

ter nor proceeds via living radical polymerization even though it contains the tetraphenylethane group in its structure. It gives benzophenone and monomer free radical in the initiation step of the polymerization of vinyl monomers [25, 26]. Hence OH groups attached to the central ethane bond of TPED play a major role in the mechanism of polymerization. In order to use the tetraphenylethane iniferter group of TPED for "living" radical polymerization, OH groups of TPED have been modified by reacting it with toluene diisocyanate [27]. It was found that the polyurethane iniferter obtained from toluene diisocyanate and TPED polymerizes vinyl monomers [28, 29] through a "living" radical mechanism. In addition, polyurethane iniferter (PIM) from diphenylmethane diisocyanate (MDI) and TPED has also been prepared and used to polymerizes acrylonitrile [30] via a "living" radical mechanism.

Braun and coworkers reported that the polymerization of methyl methacrylate (MMA) [31, 32] using tetraphenylethane derivatives follows a "living" radical mechanism whereas polymerization of styrene (ST) [32, 33] using the same type of compounds follows dead-end polymerization. Since PIM is also a tetraphenylethane derivative, it has been used to polymerize ST to check the mechanism of polymerization, and the results are discussed in this paper.

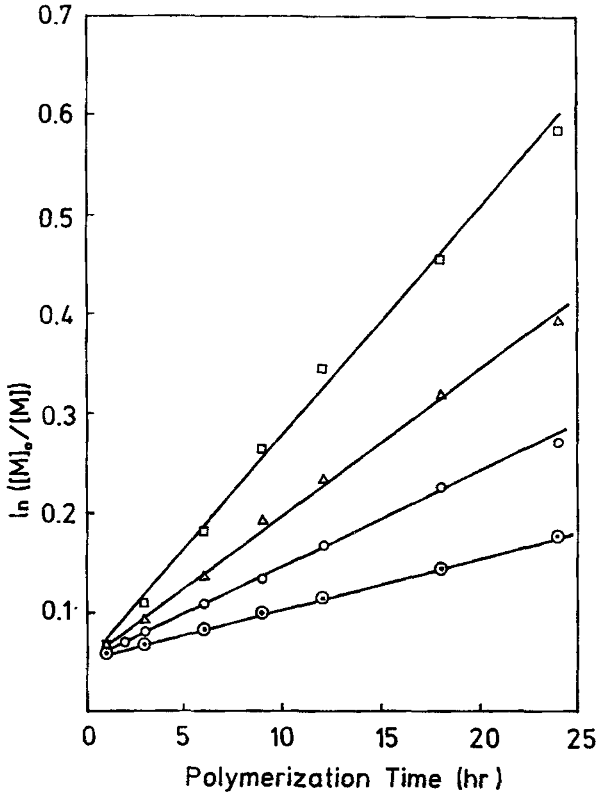


FIG. 2. Time-ln($[M]_0/[M]$) plots for ST polymerization with PIM at various temperatures. (⊙) 65°C; (○) 70°C; (△) 75°C; (□) 80°C. $[ST]_0 = 2.0$ mol/L; $[PIM]_0 = 0.02$ mol/L.

TABLE 1. "Living" Radical Polymerization of ST by PIM at 70°C in DMF[a]

No.	Time, hours	Conversion, %	GPC results $\overline{M}_n \times 10^{-3}$	 $\overline{M}_w \times 10^{-3}$	 $\overline{M}_w/\overline{M}_n$
1	1	6.05	4.96	21.52	4.34
2	2	6.87	6.35	25.01	3.94
3	3	7.75	7.32	26.86	3.67
4	6	10.25	8.77	27.62	3.15
5	9	12.57	11.60	30.27	2.61
6	12	15.50	14.68	32.88	2.24
7	18	20.32	18.57	33.98	1.83
8	24	23.74	23.41	37.46	1.60

[a] $[ST]_0 = 2.0$ mol/L; $[PIM]_0 = 0.02$ mol/L.

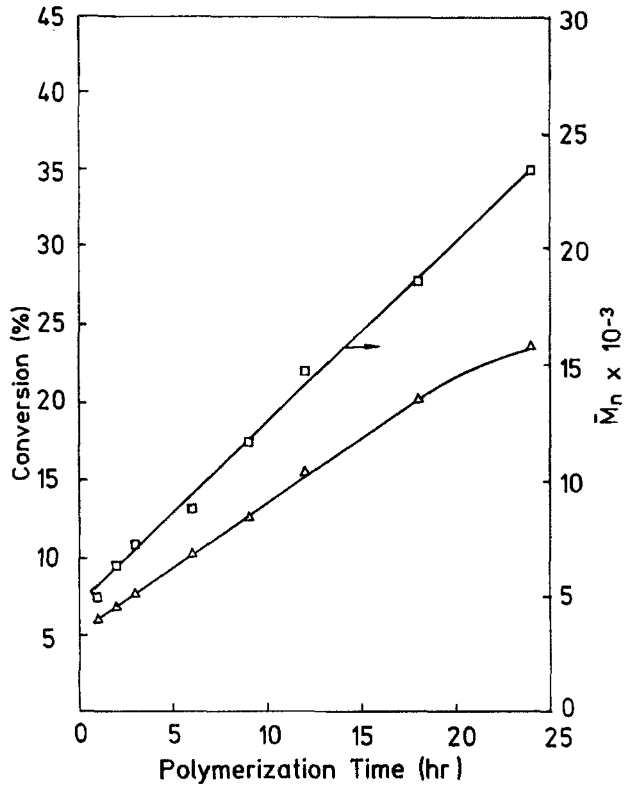


FIG. 3. Time-conversion and time-$\bar{M}_n$ relations for the polymerization of ST with PIM. $[ST]_0 = 2.0$ mol/L; $[PIM]_0 = 0.02$ mol/L.

EXPERIMENTAL

Materials

MDI (Bayer, USA) was heated at 60°C for 2 hours and filtered through a heated filter funnel before use. Dibutyltin dilaurate (DBTDL) was used as received from Aldrich, USA. Analytical grades of ST and MMA were distilled at reduced pressure after removal of inhibitor, and the middle portions were stored at 0-4°C until use. Analytical grade *N,N*-dimethylformamide (DMF) was distilled at reduced pressure, and middle portion was used after storing over molecular sieves (types 4A). The other reagents were of analytical grade and used as received.

Synthesis of TPED and PIM

TPED was prepared [34] from benzophenone and propane-2-ol. PIM was synthesized from MDI and TPED as reported earlier by us [30]. Number ($\bar{M}_n$) and weight ($\bar{M}_w$) average molecular weights and the molecular weight distribution ($\bar{M}_w/\bar{M}_n$, MWD) of MPI were determined by gel permeation chromatography (GPC), and the results were $\bar{M}_n = 1.83 \times 10^3$; $\bar{M}_w = 2.45 \times 10^3$; $\bar{M}_w/\bar{M}_n = 1.33$.

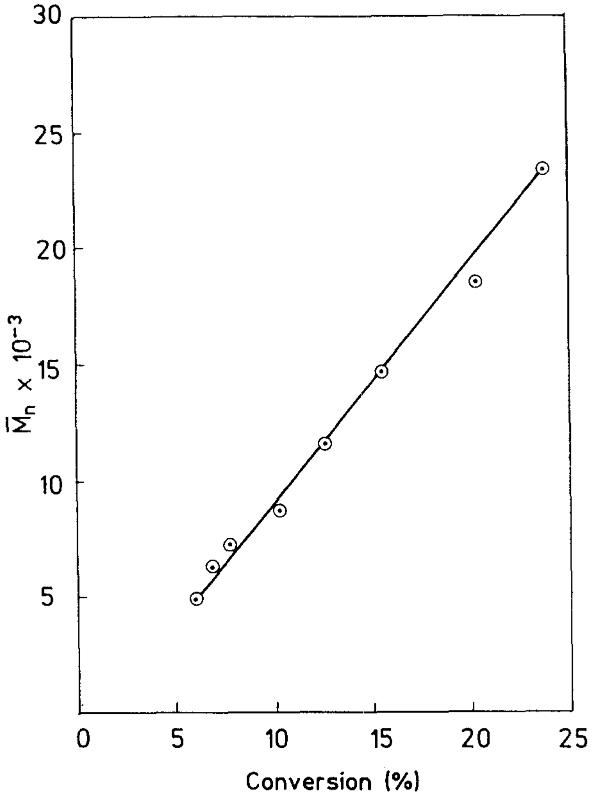


FIG. 4. Conversion-$\overline{M}_n$ plot for the polymerization of ST with PIM. $[ST]_0 = 2.0$ mol/L; $[PIM]_0 = 0.02$ mol/L.

TABLE 2. Postpolymerization of PST-PIM at 70°C in DMF[a]

		In the presence of ST			
No.	Time, hours	Yield, %	$\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
1	0	5.66	14.68	32.88	2.24
2	6	6.51	21.54	42.00	1.95
3	12	7.76	25.38	48.98	1.93
4	24	11.12	29.75	56.28	1.89
5	40	14.75	32.54	60.52	1.86

[a] $[ST]_0 = 2.0$ mol/L; $[PST\text{-}PIM]_0 = 1.25$ g/dL.

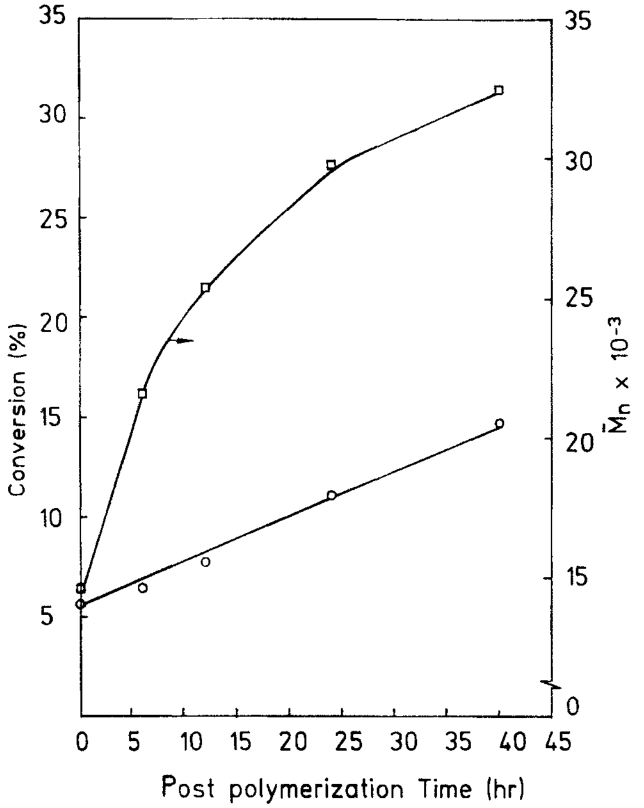


FIG. 5. Time-conversion and time-$\overline{M}_n$ relations for the postpolymerization of PST-PIM in the presence of ST. $[ST]_0 = 2.0$ mol/L; $[PST\text{-}PIM]_0 = 1.25$ g/dL.

Polymerization Procedure

Required amounts of ST, PIM [35], and DMF were charged into cylindrical Pyrex tubes, degassed by three alternate freeze-pump-thaw cycles, sealed under vacuum, and placed in a thermostated shaking water bath controlled to ±0.01°C for selected times. The tubes were then removed from the water bath after the stipulated time and the reactions were arrested by dipping in an ice-salt mixture. The resulting PST (hereinafter denoted as PST-PIM) solutions were poured into previously weighed petri dishes, the solvent evaporated, washed with methanol to remove unreacted PIM, dried in vacuum, and weighed.

The same procedure was adopted in the postpolymerization stage also, but the contents used were PST-PIM, DMF, and ST or MMA. Acetonitrile and cyclohexane were used to extract homo-PMMA and homo-PST, respectively, from block copolymers. The conversion of block copolymers was calculated in three different ways as given in Table 3.

Characterization

$\overline{M}_n$ $\overline{M}_w$, and MWDs were determined by GPC using a Waters Liquid Chromatograph equipped with a 410 differential refractometer (RI detector) and four μ-Styragel columns (10^6 Å, 10^5 Å, 10^4 Å, and 10^3 Å) in series. DMF (0.01% LiBr

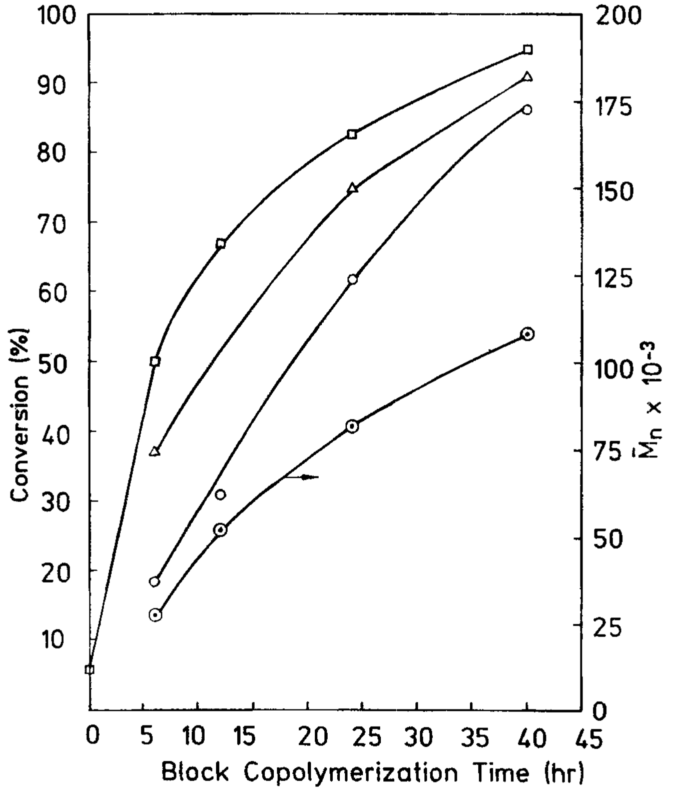


FIG. 6. Time-conversion (*Q*, *R*, and *S* from Table 3) and time-$\overline{M}_n$ (⊙) relations for block copolymerization with MMA using PST-PIM. $[\text{PST-PIM}]_0$ = 1.25 g/dL; $[\text{MMA}]_0$ = 2.0 mol/L.

added) was used as an eluent at a flow rate of 1.0 mL/min, and the molecular weight calibrations were done using polystyrene standards. The concentration and volume of polymer solutions injected were kept constant to enable comparison of the GPC curves at different polymerization times. The Fourier transform infrared (FT-IR) spectra were recorded as KBr pellets on a Nicolet Impact 400 FT-IR spectrophotometer. Fourier transform nuclear magnetic resonance (FT-NMR) spectrum of PST-PMMA block copolymer was recorded on a Bruker MSL 300 MHz NMR instrument using deuterated chloroform as the solvent. Differential scanning calorimetry (DSC) was carried out with a DuPont 910 DSC instrument at a heating rate of 10°C/min under N_2 atmosphere.

RESULTS AND DISCUSSION

Scheme 1 explains the synthetic route, structure of PIM, and the resulting structure of PST obtained from ST and PIM. Scheme 1 also explains the possible mechanism in "living" radical polymerization of ST using PIM. The synthetic route

TABLE 3. Block Copolymerization of MMA with PST-PIM at 70°C in DMF[a]

No.	Time, hours	Conversion, % Q^c	R^d	S^e	GPC results[b] $\overline{M}_n \times 10^{-3}$	$\overline{M}_w \times 10^{-3}$	$\overline{M}_w/\overline{M}_n$
1	0	5.88	–	–	–	–	–
2	6	49.86	18.48	37.07	27.94	80.19	2.87
3	12	66.87	30.92	46.24	51.67	167.41	3.24
4	24	82.46	61.85	75.00	81.55	200.62	2.46
5	40	94.71	86.11	90.92	108.46	211.50	1.95

[a] $[MMA]_0$ = 2.0 mol/L; $[PST\text{-}PIM]_0$ = 1.25 g/dL.

[b] After extraction of homopolymers, using acetonitrile and cyclohexane.

[c] $Q = \dfrac{\text{Weight of PST-PMMA block copolymers before extraction of homopolymers} \times 100}{\text{Initial weight of PST-PIM and MMA taken}}.$

[d] $R = \dfrac{\text{Weight of PST-PMMA block copolymers after extraction of homopolymers} \times 100}{\text{Initial weight of PST-PIM and MMA taken}}.$

[e] $S = \dfrac{\text{Weight of PST-PMMA block copolymers after extraction of homopolymers} \times 100}{\text{Weight of PST-PMMA block copolymers before extraction of homopolymers}}.$

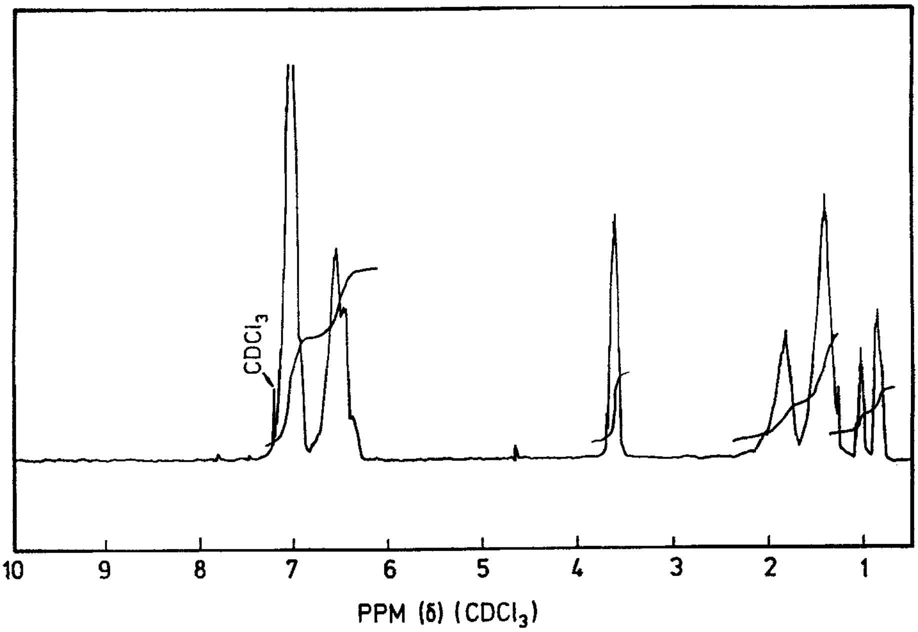


FIG. 7. ^{1}H FT-NMR spectrum of PST-PMMA block copolymer.

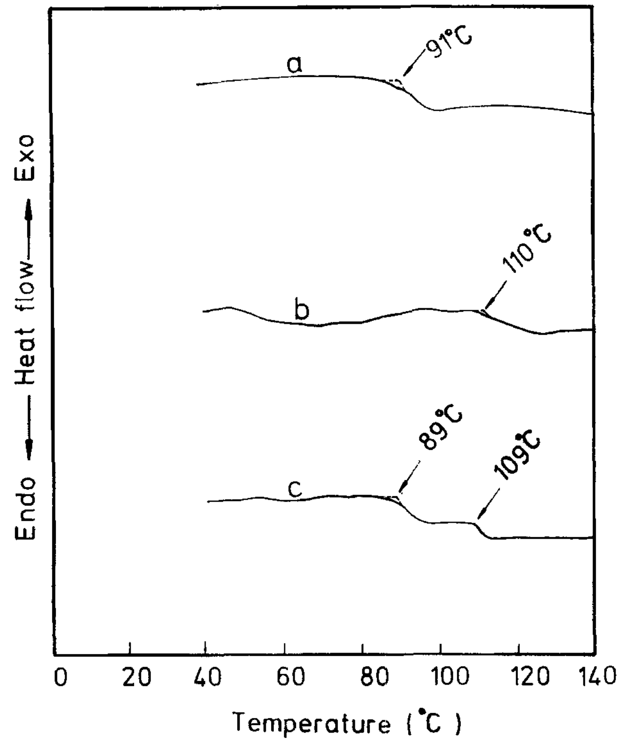


FIG. 8. DSC curves of (a) PST-PIM, (b) PMMA-PIM, and (c) PST-PMMA block copolymers.

as well as the structure of PST-PMMA block copolymers are also given in Scheme 1. Since PIM consists of tetraphenylethane groups in between organic moieties, the resulting PST-PIM is a homopolymer and the PST-PIM forms PST-PMMA block copolymer in the presence of MMA.

Figure 1 shows time-conversion plots for ST polymerization with PIM at different temperatures ranging from 65 to 80°C. Figure 2 shows the time-ln($[M]_0$/$[M]$) kinetic plots obtained for ST polymerization at different temperatures. The straight lines indicate first-order kinetics with respect to monomer. Thus, monomer is involved in the rate-limiting step. The straight lines also support the steady concentration of the active species. This result reveals that the proportion of irreversible termination is low. Table 1 gives the results of ST polymerization with PIM at 70°C in DMF. Time-conversation and time-$\overline{M}_n$ relations are shown in Fig. 3. Both conversion and $\overline{M}_n$ increase when the polymerization time increases. Figure 4 shows the conversion-$\overline{M}_n$ plot for the polymerization of ST with PIM. As the conversion increases, $\overline{M}_n$ of PST-PIM also increases. These types of results were previously obtained for "living" radical polymerization [2-5, 14-24]. Hence, even though PIM is a tetraphenylethane derivative, it follows a "living" radical mechanism and not a dead-end polymerization (as in the case of other organic tetraphenylethane-based iniferters) in the polymerization of ST.

Postpolymerization Studies

As explained in Scheme 1, if PIM polymerizes ST through a "living" radical mechanism, the PST-PIMs obtained at various polymerization times are able to undergo further polymerization. In order to check this, PST-PIM (obtained at 12 hour; cf. Table 2) was postpolymerized in the presence of MMA or ST. Figure 5 shows time-conversion and time-$\overline{M}_n$ plots for the postpolymerization of PST-PIM in the presence of ST at 70°C in DMF. As the postpolymerization time increased, both yield as well as $\overline{M}_n$ of the PST-PIM also increased in the presence of ST. Figure 6 shows time-conversion and time-$\overline{M}_n$ relations for the block copolymerization of MMA with PST-PIM. Conversion (calculated in three different ways as given in Table 3) and $\overline{M}_n$ increased with increasing block copolymerization time. These results show that the dormant PST-PIM chains cleave into active species and continue further polymerization as given in Scheme 1.

The extraction of homopolymers from crude block copolymers has been carried out using cyclohexane (for homo-PST) and acetonitrile (for homo-PMMA). Figure 7 shows the ^{1}H-NMR spectrum of the block copolymer (obtained at 24 hours; cf. Table 3). The signals at 0.80–1.1, 1.3–2.3, 3.6, and 6.33–7.1 ppm correspond to the CH_3 protons of the PMMA block, backbone CH_2 and CH protons of both blocks, $O{-}CH_3$ protons of the PMMA block, and phenyl protons of the PST block, respectively. This ^{1}H FT-NMR spectrum confirms the formation of block copolymers. The block copolymer (obtained at 24 hours; cf. Table 3) was further characterized by FT-IR and DSC techniques. The homopolymers PST-PIM (prepared at 12 hours; cf. Table 1) and PMMA (prepared in a procedure similar to PST-PIM from MMA and PIM; hereinafter referred to as PMMA-PIM) were also characterized by the same techniques for the sake of comparison. The FT-IR spectrum of PST-PMMA block copolymer exhibits the characteristic peaks at 1736 and 3084–3029 cm^{-1} which correspond to the ester carbonyl of PMMA-PIM and the —CH stretching of the benzene ring present in PST-PIM. DSC was used to determine the glass transition temperature (T_g) of the polymers, and the curves are presented in Fig. 8. The T_gs of PST-PIM, PMMA-PIM, and PST-PMMA block copolymers appeared at 91, 110, and 89°C as well as 109°C, respectively. Even though the T_gs of PMMA and PST are very close, two T_gs each for the separate blocks were obtained for the PST-PMMA block copolymer.

CONCLUSIONS

A novel polyurethane iniferter (PIM) was used to polymerize styrene. Since PIM has organic moieties in between the initiating groups, homopolystyrene was obtained. Both conversion and molecular weight increased with increasing polymerization time. Even though PIM is a tetraphenylethane derivative, it polymerizes styrene through a "living" radical mechanism. When PST-PIM was postpolymerized in the presence of ST and MMA, high molecular weight polystyrene and PST-PMMA block copolymers were obtained, respectively.

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