

Tetraphenylethane Iniferters: Polyurethane–Polystyrene Multiblock Copolymers Through “Living” Radical Polymerization

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ABSTRACT: Toluene diisocyanate-based polyurethane iniferters containing tetraphenylethane groups in between polyurethane blocks were prepared by the reaction of isocyanate-terminated prepolymers and 1,1,2,2-tetraphenyl-1,2-ethanediol. When these iniferters were decomposed in the presence of styrene, polyurethane–polystyrene multiblock copolymers were obtained through a “living” radical mechanism. The effect of changing polyol on the T_g , thermal stability, and molecular weight of polyurethane iniferters as well as block copolymers was studied. The molecular weight of the block copolymers increased with increasing both polymerization time and conversion. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1551–1560, 1997

INTRODUCTION

Polyurethane–vinyl block copolymers are speciality high-performance polymers which can be used as thermoplastic elastomers. The introduction of vinyl blocks in between polyurethane (PU) blocks can be made by reacting isocyanate-terminated prepolyurethanes and hydroxy-terminated vinyl polymers. Since vinyl blocks with the exact functionality of two are very difficult to synthesize through radical polymerization,^{1,2} a number of alternative methods are being used to synthesize PU–vinyl block copolymers. One of these methods is through macroinitiators. If the initiating groups present in between PU blocks are decomposed in the presence of vinyl monomers, PU–vinyl multiblock copolymers are obtained.

Usually, azo^{3,4}- and peroxy^{5,6}-based PU macroinitiators are used to synthesize PU–vinyl multiblock copolymers. Here, the chain length of the vinyl blocks cannot be precisely controlled. To control the chain length, molecular weight, and

molecular weight distribution (MWD) of the vinyl blocks in PU–vinyl multiblock copolymers, the iniferter technique and living radical polymerization can be used.

The concept of an iniferter⁷ and the model for living radical polymerization⁸ were proposed by Otsu et al. in 1982. Iniferter is an *initiator*, *transfer* agent, and/or *terminator* in living radical polymerization. If the polymers/oligomers obtained through iniferters initiate further polymerization of vinyl monomers, then the system is called living radical polymerization.⁸ In living radical polymerization, the chain-breaking reactions such as bimolecular irreversible termination should not occur at the complete conversion of the monomers.⁹ But it is very difficult to avoid chain-breaking reactions completely. If the chain-breaking reactions are minimum and the reversible termination is maximum, then the system is called “living” radical polymerization.⁹ Here, quotation marks denote the meager presence of chain-breaking reactions along with reversible termination.

Apart from iniferter-based “living” radical polymerization,^{8,10–12} persistent radical^{13–15} and degenerative transfer agent¹⁶-based “living” radical polymerizations are also used for controlled radi-

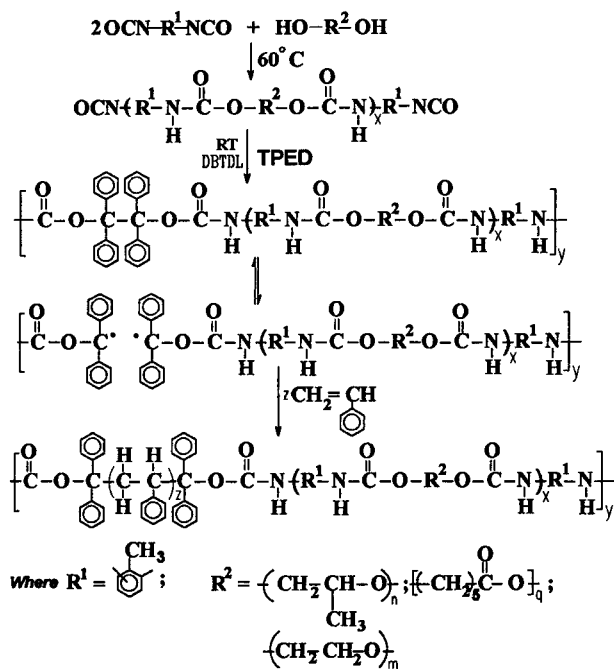
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Scheme 1

cal polymerization. Increase of the molecular weight while increasing both conversion and polymerization time is a simple evidence for "living" radical polymerization.^{8,10-16} Tetraphenylethane and disulfide derivatives are major sources of iniferters which follow "living" radical polymerization.^{8,10-12} If these iniferter groups are inserted in between PU blocks, then PU-vinyl multiblock copolymers can easily be synthesized with the desired chain length of vinyl blocks.

Tetraphenylethane groups present in between silicone blocks have been used to synthesize silicone-vinyl multiblock copolymers.^{17,18} Disulfide-based PU iniferters¹⁹ were also used to synthesize PU-vinyl multiblock copolymers. Several types of block copolymers were synthesized through macroiniferters²⁰ and the "living" radical mechanism.²¹ The potential of PUs which consist of tetraphenylethane groups have not yet been studied

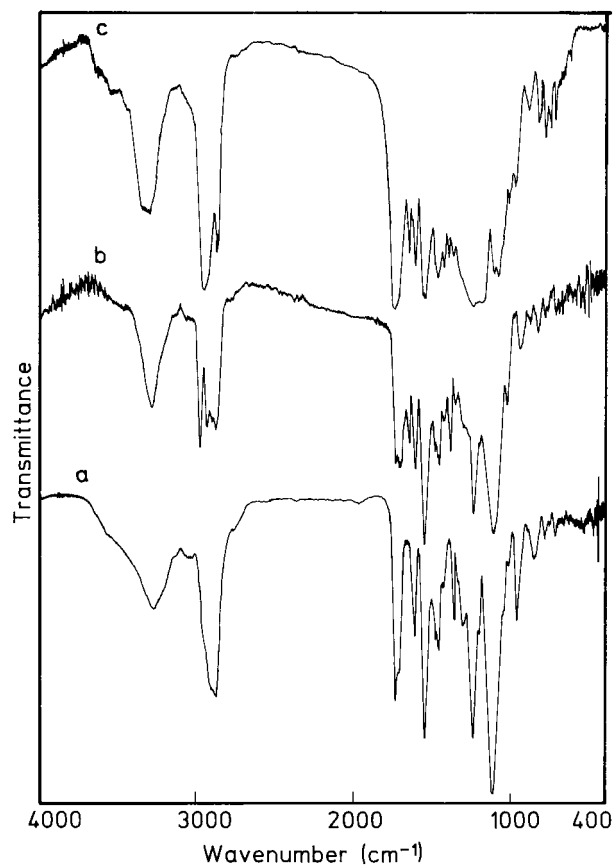


Figure 1 FTIR spectra of PU iniferters: (a) TE; (b) TP; (c) TCL.

or used for the synthesis of PU-vinyl multiblock copolymers.

In our previous article, synthesis of the PU iniferter²² (BPT) which consists of tetraphenylethane in between low molecular weight organic moieties from toluene diisocyanate and 1,1,2,2-tetraphenyl-1,2-ethanediol (TPED) was described. The "living" radical polymerization of vinyl monomers with BPT was also described.²³⁻²⁶ In this article, the synthesis and characterization of PU iniferters (which consist of tetraphenylethane groups in between PU blocks) and PU-polysty-

Table I Synthesis of PU Iniferters

Code	Prepolymer Stage		Chain Extension ^a		
	Diisocyanate (<i>M</i>)	Polyol (<i>M</i>)	TPED (<i>M</i>)	MEK (mL)	Yield (%)
TE	TDI (0.03)	PEG-1000 (0.015)	0.015	110	92.3
TP	TDI (0.03)	PPG-1000 (0.015)	0.015	120	89.2
TCL	TDI (0.012)	PCL-1250 (0.006)	0.006	70	97.8

^a DBTDL, 2 mol % based on NCO content.

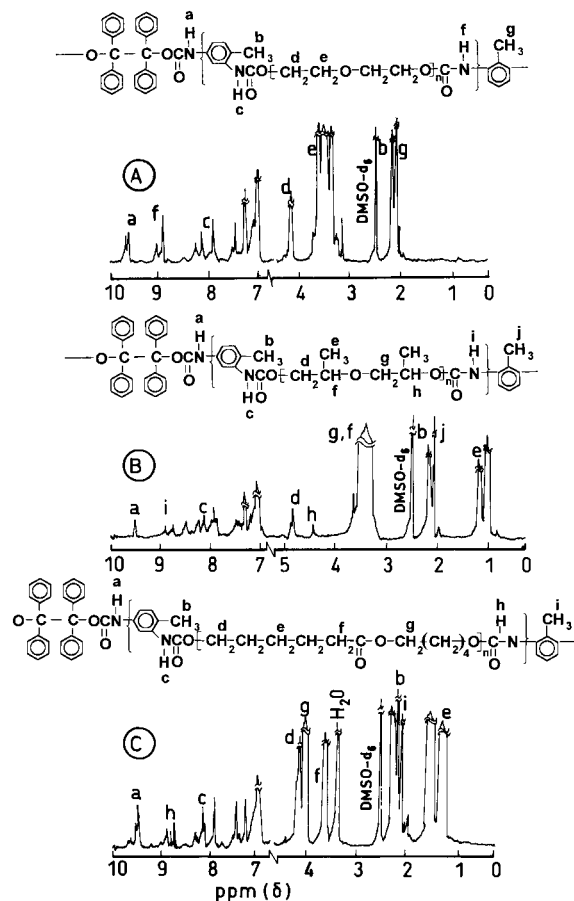


Figure 2 $^1\text{H-NMR}$ spectra PU iniferters: (a) TE; (b) TP; (c) TCL.

rene (PU–PST) multiblock copolymers from these PU iniferters are presented.

EXPERIMENTAL

Materials

Analytical-grade *N,N*-dimethylformamide (DMF) and methyl ethyl ketone (MEK) were distilled and the middle portions were used after storing over type 4 Å molecular sieves. Dibutyltin dilaur-

ate (DBTDL) and toluene diisocyanate (TDI) (mixture of 80% 2,4 and 20% 2,6 isomers) were used as received from Aldrich, U.S.A. Poly(ethylene glycol) of molecular weight 1000 (PEG-1000), poly(propylene glycol) of molecular weight 1000 (PPG-1000), and polycaprolactum diol of molecular weight 1250 (PCL-1250) (Aldrich) were used as received after drying them by heating at 105°C under a vacuum for 2 h. The inhibitor present in styrene (ST) (Aldrich) was removed by washing with 5% aqueous NaOH, washed again with distilled water, and stored over anhydrous sodium sulfate. It was then distilled at reduced pressure and the middle portion was stored at 0–4°C until use. All other chemicals used were of analytical grades and were used as received. TPED was prepared using the known method²⁷ from 2-propanol and benzophenone.

Characterization Techniques

Number-average (\bar{M}_n) and weight-average (\bar{M}_w) molecular weights and MWDs were determined by gel permeation chromatography (GPC) using a Waters liquid chromatograph equipped with a 410 differential refractometer (RI detector) and four μ -Styragel columns (10^6 , 10^5 , 10^4 , and 10^3 Å) in series. DMF (0.01% LiBr added) was used as an eluent at a flow rate of 1.0 mL/min and the molecular weight calibrations were done using PST 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 (FTIR) spectra were recorded as a KBr pellet on a Nicolet Impact 400 FTIR spectrophotometer. Fourier transform nuclear magnetic resonance (NMR) spectra were recorded on a Bruker MSLp 300 MHz NMR instrument using deuterated dimethyl sulfoxide as the solvent. Differential scanning calorimetry (DSC) analysis was carried out with a DuPont 910 DSC instrument at a heating rate of 10°C/min and thermogravimetric analysis (TGA) was carried out using DuPont 951

Table II GPC Results of PU Iniferters

PU Iniferters	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n	No. Tetraphenylethane Groups ^a
TE	2.45	2.10	14
TP	1.12	1.71	7
TCL	2.01	1.48	12

^a Values obtained by dividing \bar{M}_n by the molecular weight of the repeating unit.

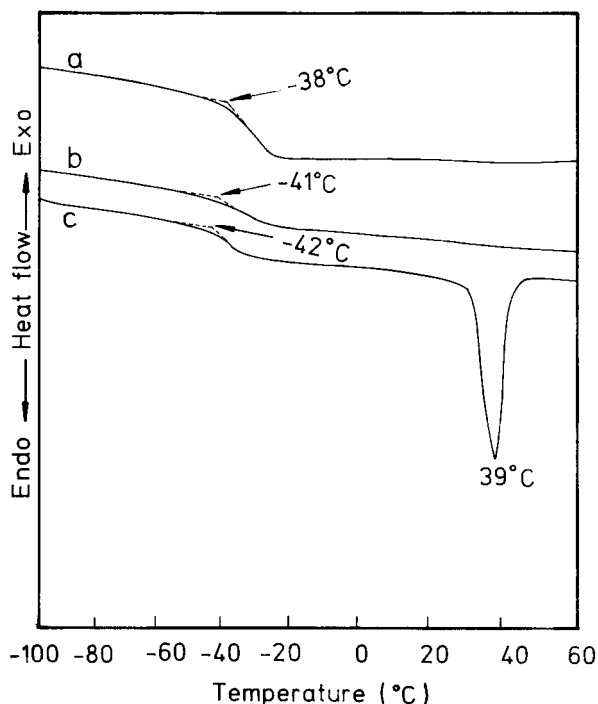


Figure 3 DSC curves of PU iniferters: (a) TE; (b) TP; (c) TCL.

TGA instrument at a heating rate of 20°C/min under a N₂ atmosphere.

General Synthetic Procedure of PU Iniferters

In a three-necked round-bottom flask, a calculated amount of previously dried polyol was taken. When the temperature reached 60°C, calculated amounts of diisocyanate were added with vigorous stirring under a nitrogen atmosphere. When the diisocyanate content reached half of the initial amount as determined by dibutylamine titration, the reaction mixture was cooled to room temperature and calculated amounts of TPED were added. To this, 2 mol % of DBTDL based on the isocyanate content was added and stirred for another 24 h at room temperature. At the end of the reaction, methanol was added to neutralize traces of the unreacted isocyanate groups and stirred for about 15 min. The resulting PU iniferter was poured into a 10-fold excess of methanol, filtered, washed thoroughly with methanol to remove unreacted TPED, dried in vacuum, and stored at 0–4°C until use.

General Synthetic Procedure of PU–PST Multiblock Copolymers

Required amounts of ST, PU iniferter, and DMF were charged into cylindrical Pyrex tubes, de-

gassed by three alternate freeze–pump–thaw cycles, sealed under a vacuum, and placed in a thermostated shaking water bath controlled to $\pm 0.01^\circ\text{C}$ 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 solutions were poured into a 10-fold excess of methanol and the precipitates were filtered, using sintered-glass crucibles, washed with methanol, dried in a vacuum, and weighed. Acetone and cyclohexane were used to extract the PUs and homo PST, respectively. Conversion was calculated in three different ways. Let us that assume X and Y are the initial weight of the PU iniferter and ST taken, respectively. If Z and M are the weight of the block copolymer obtained before and after the extraction of homopolymers, respectively, then conversion may be expressed in three different ways: viz., Q , R , and S , where $Q = Z \cdot 100/(X + Y)$; $R = M \cdot 100/(X + Y)$; and $S = M \cdot 100/Z$.

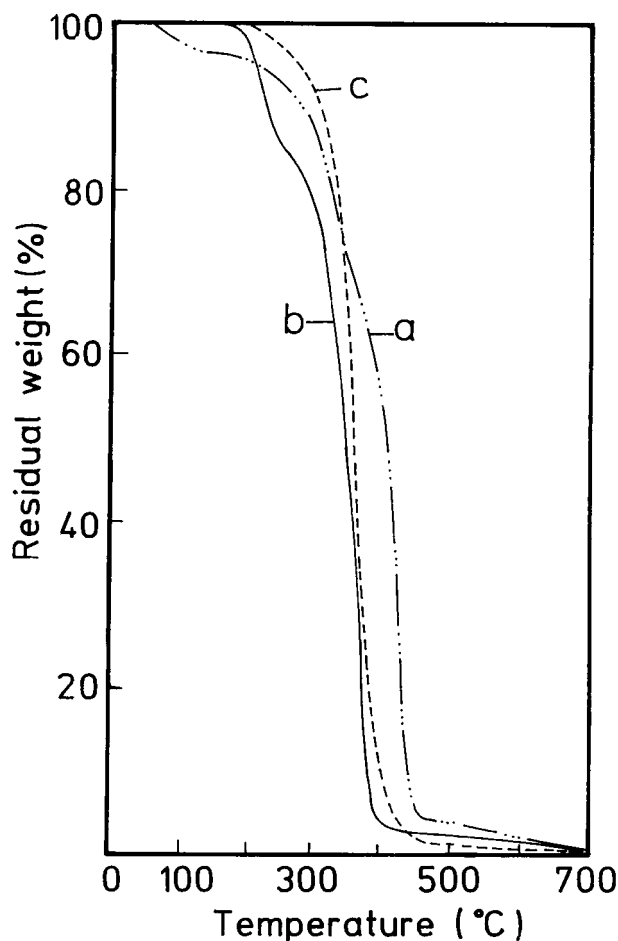


Figure 4 TGA curves of PU iniferters: (a) TE; (b) TP; (c) TCL.

Table III Block Copolymerization of ST with TE at 70°C in DMF

Sample No.	Time (h)	Conversion (%)			GPC Results ^a	
		Q^b	R^c	S^d	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n
1	0	13.05	—	—	2.45	2.10
2	1	13.28	5.25	39.54	2.62	2.24
3	3	13.73	5.85	42.61	2.93	2.42
4	6	14.28	6.65	46.58	3.18	2.36
5	9	15.45	7.67	49.64	3.42	2.34
6	12	16.37	8.83	53.94	3.73	2.32
7	18	17.42	9.65	55.37	3.98	2.31
8	24	19.53	11.59	59.36	4.17	2.30
9	36	23.62	14.63	61.94	4.55	2.15
10	48	28.88	18.04	62.46	4.62	2.02

[ST]₀ = 2.0 mol L⁻¹; [TE]₀ = 3.125 wt %.

^a After extraction of homopolymers, using acetone and cyclohexane, and the value at 0 h is for TE.

$$^b Q = \frac{\text{Weight of TE-PST multiblock copolymers before extraction of homopolymers} \times 100}{\text{Initial weight of TE and ST taken}}$$

$$^c R = \frac{\text{Weight of TE-PST multiblock copolymers after extraction of homopolymers} \times 100}{\text{Initial weight of TE and ST taken}}$$

$$^d S = \frac{\text{Weight of TE-PST multiblock copolymers after extraction of homopolymers} \times 100}{\text{Weight of TE-PST multiblock copolymers before extraction of homopolymers}}$$

RESULTS AND DISCUSSION

When the isocyanate-terminated prepolymers, prepared from excess toluene diisocyanate and polyols, are chain-extended with TPED, PU iniferters containing tetraphenylethane groups in between the PU blocks are obtained. When these macroiniferters are decomposed in the presence of ST, PU-PST multiblock copolymers are obtained. Scheme 1 explains the general synthetic route and structures of PU iniferters as well as of PU-PST block copolymers.

Synthesis and Characterization of PU Iniferters

The details of synthesis of the PU iniferters are given in Table I. Figure 1 shows the FTIR spectra of PU iniferters. The characteristic peaks of carbonyl stretching of urethane groups present in the PU iniferters are observed at about 1700 cm⁻¹. The peak at about 3300 cm⁻¹ corresponds to N-H stretching vibrations. The peaks corresponding to aliphatic -CH₂ stretching vibrations appeared at about 2900 cm⁻¹. Figure 2 shows the ¹H-NMR spectra of PU iniferters. The N-H protons of urethane linkages present in PU iniferters are observed at about 8.1, 8.8, and 9.5 ppm. The -CH₃ protons from TDI units are observed as a

doublet at 2.0 and 2.1 ppm. The peaks corresponding to aromatic protons from TPED and TDI units are observed between 7 and 7.5 ppm. The -O-CH₂ and protons in PEG units appear at 3.3–3.6 ppm. The -O-CH₂ and -OCH- protons in PPG-based iniferters adjacent to urethane groups are observed at about 5 and 4.5 ppm, respectively. The -CH₃ and -O-CH protons of the PPG unit are observed at about 1.1 and 3.3–3.6 ppm, respectively. The -CH₂ protons of PCL are observed at 1.3–1.57 ppm. The peak corresponding to -O-CH₂ groups adjacent to the urethane groups present in TE appears at about 4.1 ppm. The -CH₂ protons corresponding to ester groups of the PCL unit and that of the urethane units are merged and a broad peak is observed at 4.1 ppm. The CH₂ protons adjacent to C=O of the ester groups of PCL appeared at 3.6 ppm. All the methylene protons adjacent to ether linkages (-O-CH₂-) which resonate around 3.3 ppm merge with the water signal present in the DMSO-*d*₆ solvent, leading to broadening of the peak here. Table II gives the GPC results of PU iniferters. In the PPG-based macroiniferter (TP), since one of the hydroxyl end groups is primary and the other is secondary (which is less reactive when compared to other polyols), the molecular weight of this iniferter is lower than that of the other iniferters. The number of tetraphenyl-

Table IV Block Copolymerization of ST with TP at 70°C in DMF

Sample No.	Time (h)	Conversion (%)			GPC Results ^a	
		Q^b	R^c	S^d	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n
1	0	13.05	—	—	1.12	1.71
2	1	13.52	7.34	54.32	1.20	1.76
3	3	13.93	8.34	59.84	1.25	1.82
4	6	14.68	9.89	67.37	1.28	1.89
5	9	16.84	11.93	75.34	1.33	1.92
6	12	17.06	13.93	81.64	1.39	2.12
7	18	18.93	16.59	87.64	1.47	2.64
8	24	20.47	18.36	89.67	1.54	2.84
9	36	23.18	21.19	91.42	1.50	3.12
10	48	26.49	24.49	92.46	1.74	3.23

[ST]₀ = 2.0 mol L⁻¹; [TP]₀ = 3.125 wt %.

^a After extraction of homopolymers, using acetone and cyclohexane, and the value at 0 h is for TP.

$$^b Q = \frac{\text{Weight of TP-PST multiblock copolymers before extraction of homopolymers} \times 100}{\text{Initial weight of TP and ST taken}}$$

$$^c R = \frac{\text{Weight of TP-PST multiblock copolymers after extraction of homopolymers} \times 100}{\text{Initial weight of TP and ST taken}}$$

$$^d S = \frac{\text{Weight of TP-PST multiblock copolymers after extraction of homopolymers} \times 100}{\text{Weight of TP-PST multiblock copolymers before extraction of homopolymers}}$$

ethane groups present in the macroiniferters is also given in Table II. When the molecular weights of the iniferters are divided by the molecular weight of their corresponding repeating units, the number of tetraphenylethane groups present in the particular macroiniferter can be obtained. Even though these values are approxi-

mate, they are useful to understand the effectiveness of the macroiniferters. Figure 3 shows the DSC curves and T_g values of the PU iniferters. The low T_g values obtained for all the PU iniferters is characteristic of the polymer. Figure 4 shows TGA curves of the PU iniferters. The order of thermal stability is TP < TCL < TE.

Table V Block Copolymerization of ST with TCL at 70°C in DMF

Sample No.	Time (h)	Conversion (%)			GPC Results ^a	
		Q^b	R^c	S^d	$\bar{M}_n \times 10^{-4}$	\bar{M}_w/\bar{M}_n
1	0	13.05	—	—	2.01	1.48
2	1	13.74	5.68	41.35	2.16	1.94
3	3	14.27	6.60	46.64	2.46	2.69
4	6	15.21	7.86	51.69	2.87	2.82
5	9	16.19	9.34	57.67	3.38	2.53
6	12	17.39	10.98	63.16	3.83	2.51
7	18	18.88	12.76	67.58	4.23	2.49
8	24	20.34	14.78	71.69	4.67	2.34
9	36	23.53	17.63	74.92	4.90	2.26
10	48	27.85	21.79	78.25	5.29	2.12

[ST]₀ = 2.0 mol L⁻¹; [TCL]₀ = 3.125 wt %.

^a After extraction of homopolymers, using acetone and cyclohexane, and the value at 0 h is for TCL.

$$^b Q = \frac{\text{Weight of TCL-PST multiblock copolymers before extraction of homopolymers} \times 100}{\text{Initial weight of TCL and ST taken}}$$

$$^c R = \frac{\text{Weight of TCL-PST multiblock copolymers after extraction of homopolymers} \times 100}{\text{Initial weight of TCL and ST taken}}$$

$$^d S = \frac{\text{Weight of TCL-PST multiblock copolymers after extraction of homopolymers} \times 100}{\text{Weight of TCL-PST multiblock copolymers before extraction of homopolymers}}$$

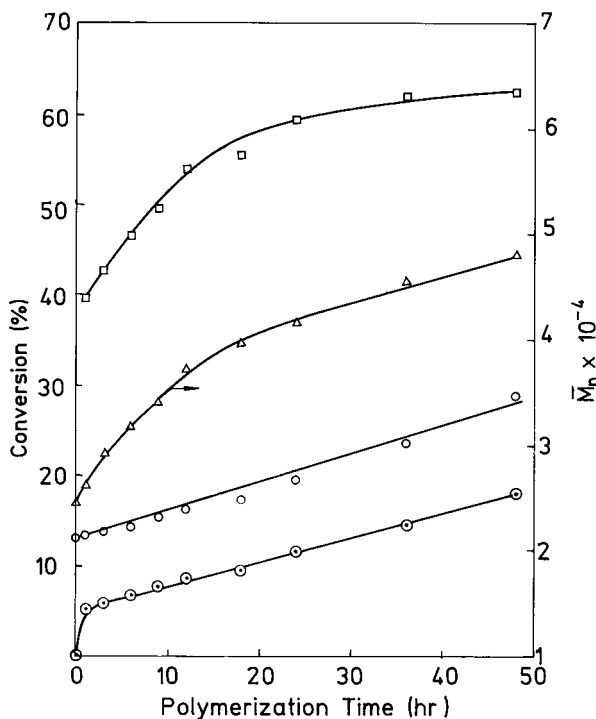


Figure 5 Time-conversion [(○) Q, (⊙) R, and (□) S from Table III] and (Δ) time- \bar{M}_n relations for the polymerization of ST by TE in DMF at 70°C; $[\text{TE}]_0 = 3.125 \text{ wt } \%$; $[\text{ST}]_0 = 2.0 \text{ mol L}^{-1}$.

Synthesis and Characterization of PU-PST Multiblock Copolymers

Results from Tables III-V show that the PU iniferters initiate ST and form PU-PST multiblock copolymers as given in Scheme 1. The PU-PST multiblock copolymers that form TE, TP, and TCL are hereinafter referred to as TE-PST, TP-PST, and TCL-PST, respectively. Figures 5-7 show the time-conversion and time- \bar{M}_n relations for the polymerization of ST by PU iniferters. In all these systems, both conversion (calculated in three different ways as given in the Experimental part) and \bar{M}_n increase with increasing polymerization time. This is a typical result for "living" radical polymerization.^{8,10-12,23-26} Hence, the PU iniferters (TE, TP, and TCL) polymerize ST through a "living" radical polymerization. Figure 8 gives the conversion- \bar{M}_n plot for the polymerization of ST by TE, TP, and TCL. Here, the conversion R (cf. Tables III-V) is plotted against the \bar{M}_n of the block copolymers. It is well known that the molecular weight does not increase with increasing conversion in the conventional free-radical polymerization, whereas in the case of living polymerizations, the molecular weight increases with increase in conversion.²⁸ In this case also, as

the conversion increases, \bar{M}_n also increases, showing that the polymerization proceeds via a "living" radical mechanism.^{11-14,16,18} Since the molecular weight of the PU iniferters increase in the order TP < TCL < TE (cf. Table II), the molecular weight of the resulting multiblock copolymers are also in the order TP-PST < TCL-PST < TE-PST (cf. Table III-V).

In GPC, both unimodal^{2,16,18} and bimodal^{10,14,23-26} peaks are obtained for "living" radical polymerization. When the iniferter starts the polymerization, first, low molecular weight polymers are obtained due to the primary radical termination. In the second step, the polymers formed initiate further polymerization to give high molecular weight polymers. If the molecular weight difference between the first and the second stage is higher, bimodal peaks are obtained, whereas if this difference is lower, unimodal peaks are obtained. In our previous articles,²³⁻²⁶ when the low molecular weight PU iniferters (from 1 : 1 reaction of TDI and TPED) were used to polymerize vinyl monomers (AN, MMA, and ST), bimodal peaks were obtained in GPC.

Figure 9 shows the GPC curves obtained for the polymerization of ST by TE. For comparison,

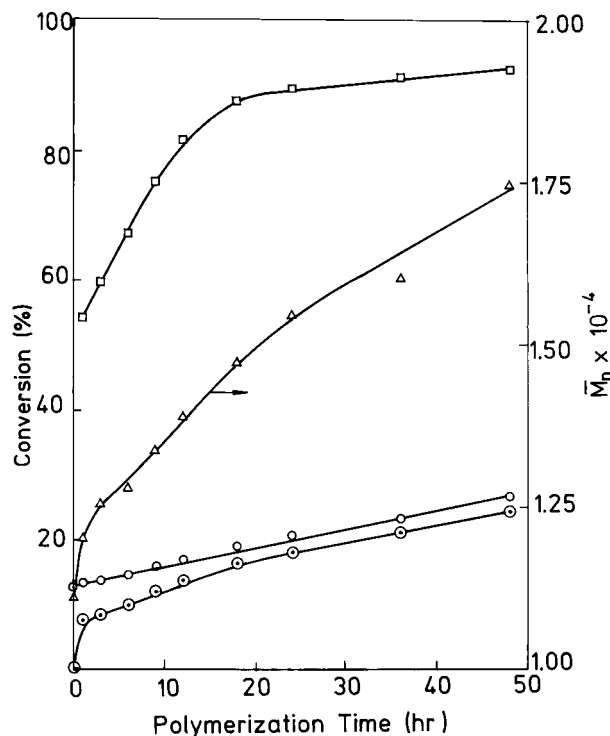


Figure 6 Time-conversion [(○) Q, (⊙) R, and (□) S from Table IV] and (Δ) time- \bar{M}_n relations for the polymerization of ST by TP in DMF at 70°C; $[\text{TP}]_0 = 3.125 \text{ wt } \%$; $[\text{ST}]_0 = 2.0 \text{ mol L}^{-1}$.

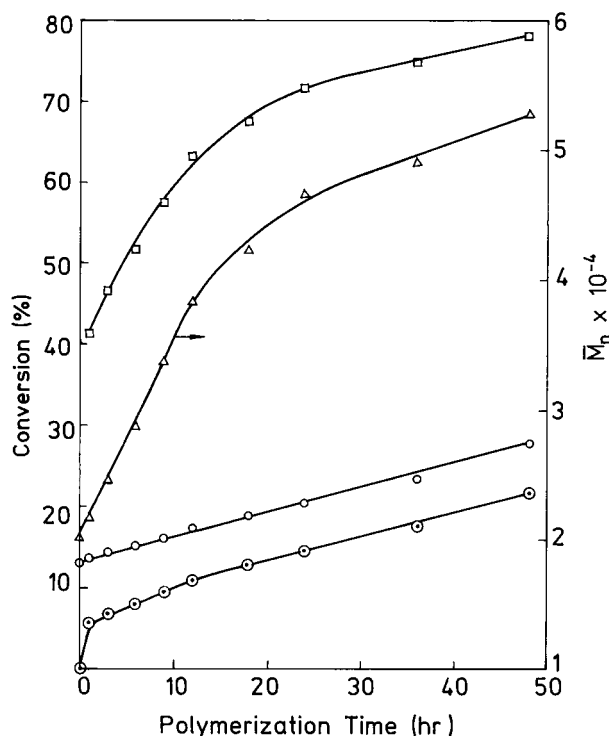


Figure 7 Time-conversion [(○) Q, (○) R, and (□) S from Table V] and (△) time- \bar{M}_n relations for the polymerization of ST by TCL in DMF at 70°C; $[\text{TCL}]_0 = 3.125 \text{ wt } \%$; $[\text{ST}]_0 = 2.0 \text{ mol}^{-1} \text{ L}^{-1}$.

the GPC curve of TE is also given at 0 h. The same type of peaks were obtained for TCL-PST multiblock copolymers. Figure 10 shows GPC curves of the TP-PST multiblock copolymers. It is interesting to note that the multiblock copolymers obtained from the low molecular weight macroiniferter, namely, TP (cf. Fig. 10), gives bimodal peaks, whereas the block copolymers obtained from other macroiniferters give an unimodal distribution. As explained earlier, the low molecular weight macroiniferter from both low and high molecular weight polymers, thereby showing a bimodal distribution, whereas high molecular weight iniferters form high molecular weight polymers only and therefore unimodal peaks were observed.

In the bimodal GPC curves, as the polymerization time increases, the peak corresponding to high molecular weight portions also increase (cf. Fig. 10). In the unimodal GPC curves as the polymerization time increases, the peaks shift to a lower elution volume side, i.e., the high molecular weight side.

To confirm the structures of PU-PST multiblock copolymers, the polymers obtained at 48 h (cf. Tables III-V) are characterized by FTIR and

$^1\text{H-NMR}$ spectroscopy. When compared with the FTIR spectra of their respective iniferters (Fig. 1), we found that the intensities of the $-\text{CH}$ stretching vibrations of the benzene ring at 3098, 3065, and 3032 cm^{-1} are increased in the FTIR spectra of multiblock copolymers. This result shows that the PST units are present in the PU-PST multiblock copolymers. To confirm further, the $^1\text{H-NMR}$ spectra of the PU-PST multiblock copolymers were recorded. In addition to the peaks of the PU iniferters, the peaks corresponding to the backbone $-\text{CH}_2$ and $-\text{CH}$ protons of PST resonate between 1.3 and 2.3 ppm. As a representative to other block copolymers, the $^1\text{H-NMR}$ spectra of TE-PST multiblock copolymer prepared at 48 h (cf. Table III) is given in Figure 11.

Block copolymers obtained at 48 h (cf. Tables III-V) are used for DSC studies. Figure 12 gives the DSC curves and T_g values of PU-PST multiblock copolymers. In addition to the glass transition temperatures of PU blocks, the T_g of PST appears at 111°C for TE-PST as well as for TP-PST multiblock copolymers and at 109°C for TCL-PST multiblock copolymers. The T_g of the

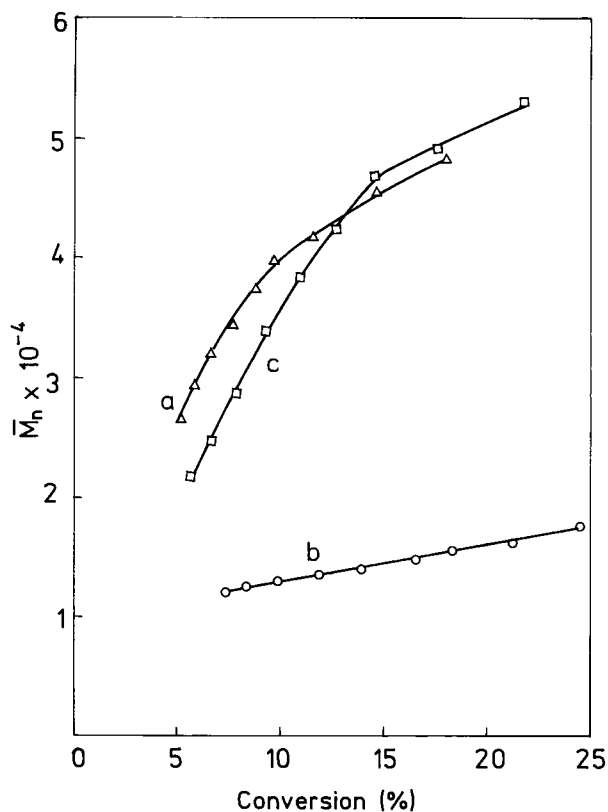


Figure 8 Conversion- \bar{M}_n plots for the polymerization of ST by PU iniferters: (a) TE-PST; (b) TP-PST; (c) TCL-PST; $[\text{TE}]_0 = [\text{TP}]_0 = [\text{TCL}]_0 = 3.125 \text{ wt } \%$; $[\text{ST}]_0 = 2.0 \text{ mol L}^{-1}$.

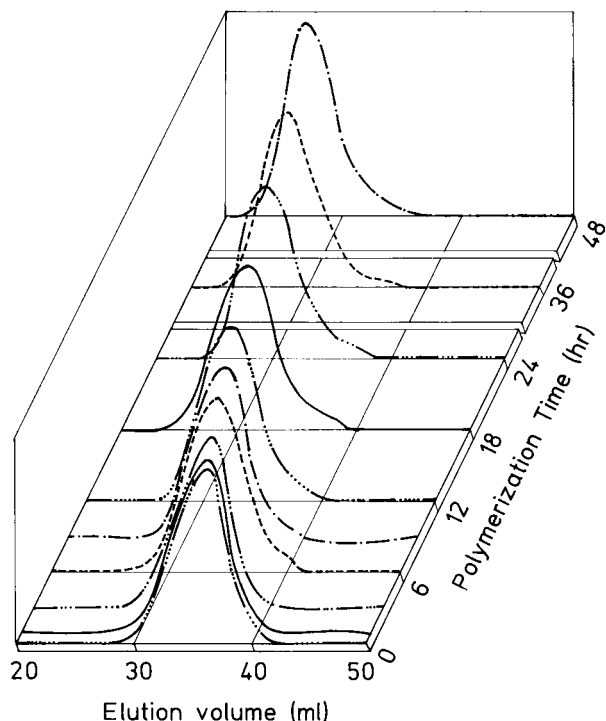


Figure 9 GPC curves for the polymerization of ST by TE in DMF at 70°C; $[TE]_0 = 3.125$ wt %; $[ST]_0 = 2.0$ mol L⁻¹.

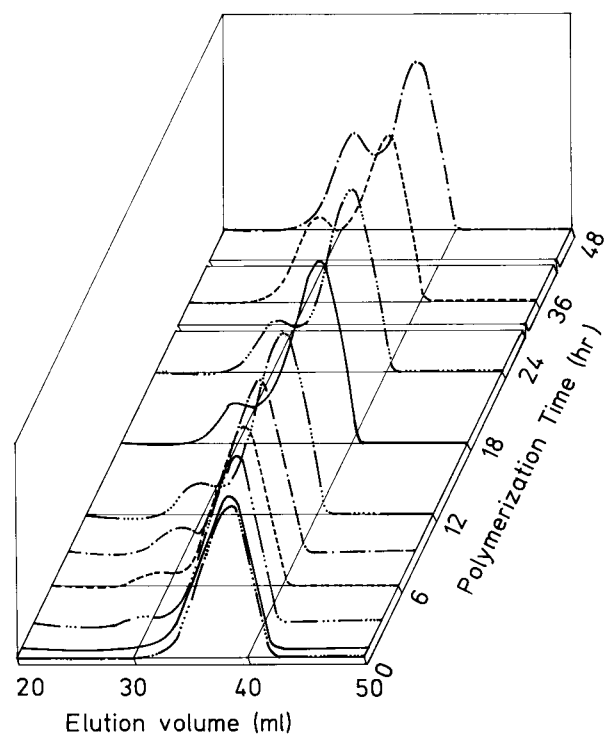


Figure 10 GPC curves for the polymerization of ST by TP in DMF at 70°C; $[TP]_0 = 3.125$ wt %; $[ST]_0 = 2.0$ mol L⁻¹.

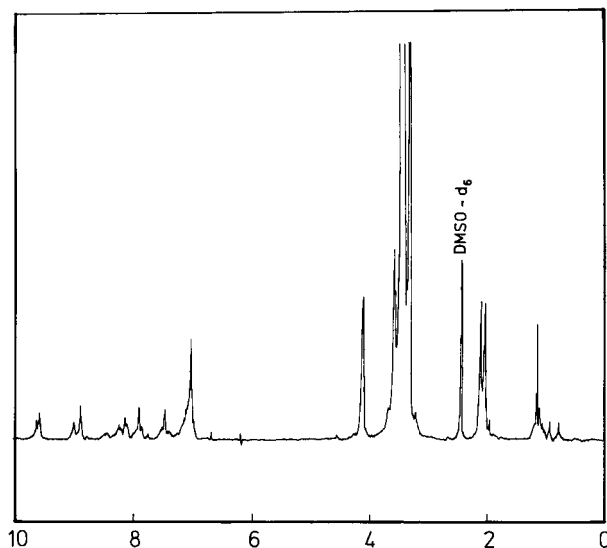


Figure 11 ¹H-NMR spectrum of the TE-PST multiblock copolymer.

PU segment shifts to higher temperature in the PU-PST multiblock copolymers when compared to their parent PU iniferters (cf. Fig. 3).

Figure 13 gives the thermal stability of PU-PST multiblock copolymers. The order of the thermal stability is TCL-PST ≤ TP-PST < TE-PST. Almost a similar type of result is observed in the thermal stability of their respective parent PU iniferters (cf. Fig. 4).

CONCLUSION

The novel PU iniferters were prepared from TDI, polyols, and TPED. When these PU iniferters were decomposed in the presence of ST, PU-PST

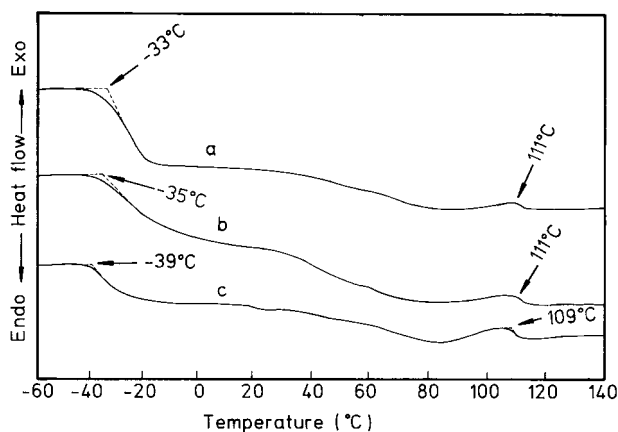


Figure 12 DSC curves of PU-PST multiblock copolymers: (a) TE-PST; (b) TP-PST; (c) TCL-PST.

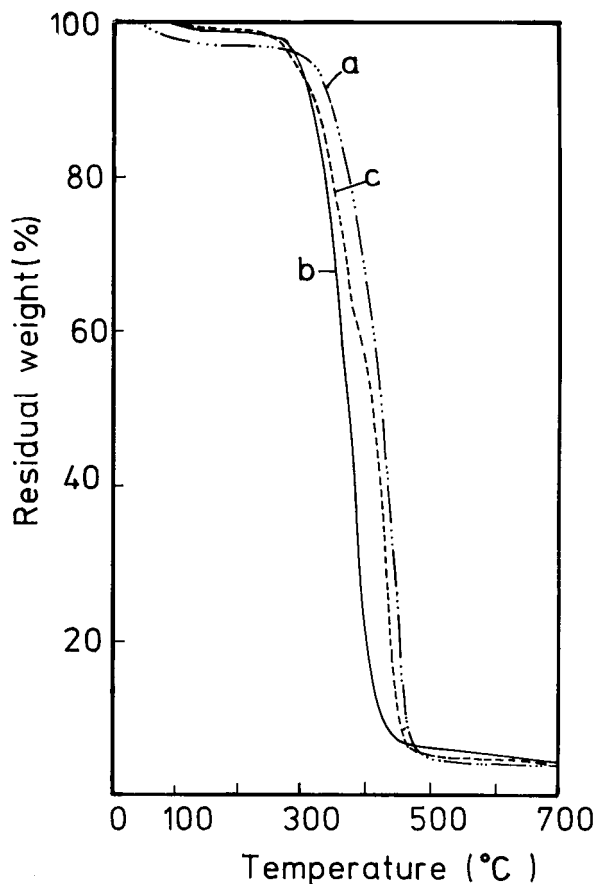


Figure 13 TGA curves of PU-PST multiblock copolymers: (a) TE-PST; (b) TP-PST; (c) TCL-PST.

multiblock copolymers were obtained. Multiblock copolymers from a low molecular weight PU iniferter give bimodal peaks, whereas multiblock copolymers from high molecular weight PU iniferters give unimodal peaks in GPC. DSC studies of multiblock copolymers show the T_g s of both PU and PST segments.

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