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Polystyrene-b-polydimethyl siloxane (PDMS) multicomponent polymer networks: styrene polymerization with macromonomeric initiators (macroinimers) having PDMS units

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A new macromonomeric initiator (macroinimer) was synthesized and evaluated for the bulk polymerization of styrene at 60 and 80°C. The macroinimer containing poly(dimethylsiloxane), PDMS, was synthesized via condensation reactions between 4,-4′-azobis-4-cyanopentanoyl chloride (ACPC), PDMS and methacryloyl chloride. The product (MIM I) was thermally homopolymerized and copolymerized with styrene in bulk. Kinetics of radical polymerization of styrene with MIM I at 60°C and at low conversion was studied. Rate constant K, $k_p(fk_d/k_t)^{1/2}$, was estimated from kinetic data as $1.15 \times 10^{-4}\ l^{1/2}\ mol^{-1/2}\ s$. Bulk polymerization of styrene with macroinimers at 80°C gave crosslinked block copolymers. D.s.c. measurements showed that crosslinked block copolymers had a glass transition temperature around 45°C. This is evidence of a plasticizing effect of flexible polysiloxane segments in copolymers. Crosslinked PDMS-b-PS block copolymers obtained using macroinimers may be an interesting group of thermoplastic elastomers. © 1997 Elsevier Science Ltd.

(Keywords: macroinimer; poly(dimethylsiloxane); poly(S-b-PDMS) polymer network)

INTRODUCTION

A variety of macroinitiators, macromonomers (macromers) and macromonomeric initiators (macroinimers) have been reported for the synthesis of block and graft copolymers[1–5]. It was recently reported that crosslinked block copolymers of styrene containing polyethyleneglycol (PEG) units could be prepared with macroinimers[6]. Macroinimers behave as macroinitiators, macromonomers and macrocrosslinkers in thermal polymerization by themselves or copolymerization with a vinyl monomer.

Block and graft copolymers of conventional vinyl polymers with polysiloxanes may be an interesting group of thermoplastic elastomers with some excellent properties, such as low glass transition temperature, high thermal stability, low surface energy, high gas permeability, etc.[7,8]. Macro-azo-initiators containing polydimethylsiloxane (PDMS) segments were proposed to be interesting intermediates for the synthesis of block and graft copolymers via radical process. In our previous work[9], block and graft copolymers of polystyrene and polybutadiene were synthesized using PDMS containing macro-azo-initiator. In the present study, attempts were made to synthesize new macromonomeric initiator (macroinimer) having poly(dimethylsiloxane) units according to *Scheme 1*. Kinetics of bulk polymerization of styrene with MIM I at low conversions and crosslinking of styrene were studied. Thermal properties of crosslinked PDMS-b-PS copolymers were compared with the copolymers of styrene prepared by macro-azo-initiators of PDMS.

EXPERIMENTAL

Materials

4,4′-Azobis-4-cyanopentanoic acid (ACPA) and methacryloyl chloride were supplied from Fluka AG. 4,4′-Azobis-4-cyanopentanoyl chloride (ACPC) was synthesized from ACPA reacted with PCl_5[9,10]. α-ω-Amine terminated poly(dimethylsiloxane), PDMS was kindly supplied from Goldschmidt Chemical Corp. (ASI-2120) with M_n 1050 g mol^{-1}. Styrene was obtained from Fluka AG. It was free from inhibitor by washing 5% NaOH solution and distilled water. It was dried with Na_2SO_4 and freshly distilled under reduced pressure before use. Solvents and other reagents were extra pure commercial products.

Synthesis of macroinimer (macromonomeric initiator)

Macroinimer (MIM I) containing PDMS units was synthesized. The steps in the reaction and the products obtained can be seen in *Scheme 1*.

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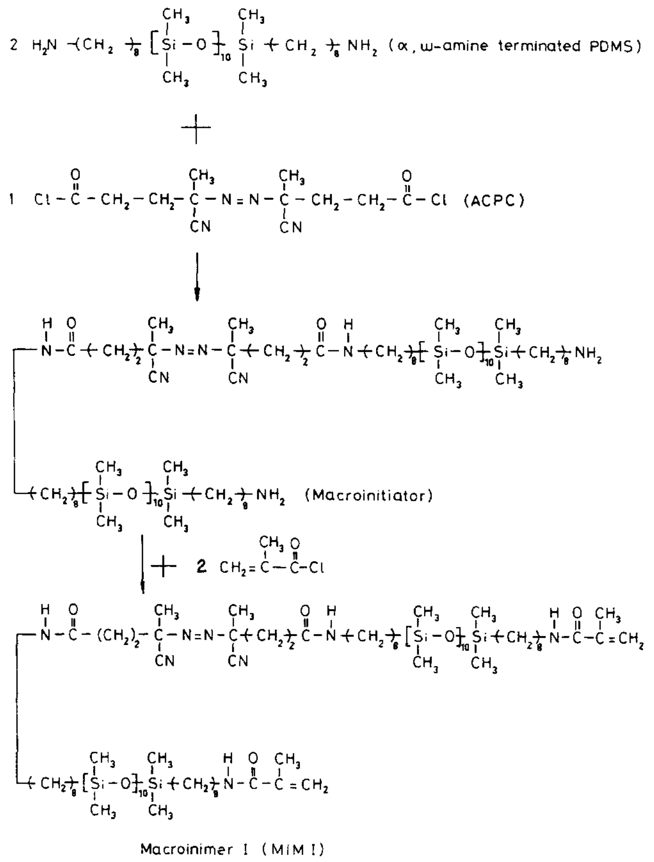

Scheme 1

Synthesis of MIM I. In a typical procedure for MIM I, a solution of 9.5 mmol ACPC in 50 ml CCl_4 was added to 19 mmol α-ω-amine terminated PDMS prepolymer and 50 ml (5 wt%) aqueous NaOH solution. The reaction mixture was stirred for 24 h at room temperature. The molar ratio of ACPC to PDMS was 1 : 2. After the reaction, the mixture was washed with water three times to eliminate salts and ACPA from the product. The organic phase was dried with Na_2SO_4 by allowing to stand in a refrigerator overnight. After filtering and evaporation, yellow viscous liquid (macroinitiator) was dried and stored in a refrigerator until use.

The second step in the synthesis of MIM I is the addition of methacryloyl chloride into the macroinitiator obtained. The yellow viscous liquid in 50 ml aqueous NaOH solution (5 wt%) was mixed with methacryloyl chloride in CCl_4. The molar ratio of macroinitiator to methacryoyl chloride was 1/3. The reaction mixture was stirred for 24 h and after reaction the mixture was washed with water and the product (MIM I) was dried with Na_2SO_4. After evaporation of solvent, it was dried and stored in a refrigerator. The yield was 90.5%. *Table 1* shows the preparation conditions and the characterization of macroinimer, MIM I.

Homopolymerization of macroinimer

Macroinimer, MIM I was thermally homopolymerized at 60, 70 and 80°C for 5 h. It gave crosslinked PDMS in different yields (23, 52 and 64 wt%, respectively). MIM I was also homopolymerized at constant temperature (80°C) for various reaction times (1–24 h). The soluble part was extracted from network polymer by soaking in $CHCl_3$ overnight at room temperature.

Bulk polymerization and crosslinking of styrene with macroinimer

Calculated amounts of macroinimer (MIM I) and styrene were introduced into pyrex reaction tubes and nitrogen was introduced through a needle into the tube to expel the air. The tightly capped tube containing a small magnet was put in an oil bath on a magnetic stirrer at 60 or 80°C for various reaction times. The reaction mixture was poured into a large amount of methanol to precipitate the product and the precipitate was collected by filtration and dried under vacuum. Conversions were kept below 17% by weight for kinetic analysis of the data at 60°C. Polymerization of styrene with macroinimer at 80°C for higher conversion ($\geq$ 47 wt%) gave crosslinked products.

Characterization

Number average molecular weights (M_n) of MIM I was determined with a Knauer Vapor Pressure Osmometer at 25°C in CH_2Cl_2. The calibration of M_n was made by a benzil standard with M_n of 210.23.

Measurement of the number of vinyl end groups of MIM I was carried out by bromometry using pyridine sulfate dibromide reagent (PSDB) in glacial acetic acid. The method is based on the reaction of vinyl groups with bromine produced *in situ* for the PSDB reagent and back-titration of the excess bromine and from various titration methods, bromination with PSDB is reported to be capable of very accurate results[11,12].

Gel permeation chromatography (g.p.c.) was used to determine molecular weights and their distributions with a Waters instrument (410 Differential Refractometer) in THF. The elution rate was 1 ml min^{-1}. Waters Styragel columns HR1 and HT6E were used and molecular weights were calibrated with polystyrene standards (TOSOH Corp.).

I.r. spectra of MIM I and polymer samples were taken using a Perkin-Elmer 177 IR spectrometer. ^1H n.m.r. spectra of the products were recorded using a Bruker-AC 200 L, 200 MHz n.m.r. spectrometer.

The swelling of the crosslinked polymer samples was carried out by storing 0.3 g of the samples in 50 ml of $CHCl_3$ for 24 h at r.t. The swelling ratio, Q, was calculated by the following equation[13]:

$$Q = (V_{\text{dry polymer}} + V_{\text{solvent}})/V_{\text{dry polymer}}$$

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

D.s.c. thermograms were taken on a DuPont DSC-910 model apparatus at a heating rate of 10°C min^{-1}. The glass transition temperature (T_g) was taken at the onset of the corresponding heat capacity jump.

RESULTS AND DISCUSSION

Macroinimer

Reaction *Scheme 1* was followed in the synthesis of macroinimer, MIM I. *Table 1* shows the synthesis conditions and results of reactions between PDMS, ACPC and methacryloyl chloride. The number average molecular weights (M_n) determined by vapour pressure osmometry indicates that the reactions proceed almost quantitatively, with yields of 90.5 wt%. Measurement of vinyl end groups of macroinimer was also attempted by ^1H n.m.r.[12]. A typical n.m.r. spectrum of macroinimer

Table 1 Preparation conditions and characterization of macroinimer (MIM I)

Macroinimer	$R \times n$ steps	PDMS[a] g	PDMS[a] mmol	NaOH soln (5 wt%) (ml)	ACPC[b] g	ACPC[b] mmol	CCl_4 (ml)	Meth. chl.[c] g	Meth. chl.[c] mmol	M_n (VPO) ($g\,mol^{-1}$)	Number of vinyl groups per mol
MIM I	1	19.95	19.0	50	3.01	9.5	50			1800	1.90
	2						50	3.07	29.4	2424ca	

[a] PDMS prepolymer, α-ω-amine terminated, $M_n = 1050\,g\,mol^{-1}$
[b] 4,4′-Azobis-4-cyanopentanoyl chloride
[c] Methacryloyl chloride

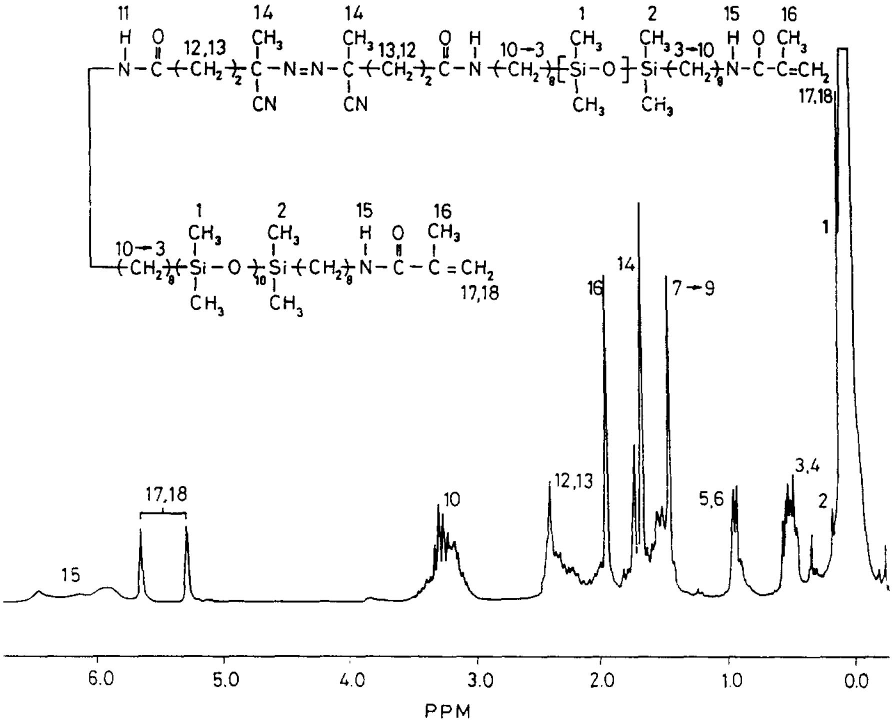

Figure 1 ^1H n.m.r. spectrum of the macroinimer (MIM I)

(MIM I) is shown in *Figure 1*. Characteristic shifts of vinylic protons were at 5.28 and 5.65 ppm. The ratio of areas under the peaks of vinylic protons to the methyl proton at 1.94 ppm was found to confirm the structural formula. In *Figure 1*, we observed shifts, δ ppm, of $-CH_2$ groups (at δ 2.21–2.39) and $-CH_3$ groups (at δ 1.62–1.72) of ACPC. The signals at δ 5.9 and 6.4 are due to $-NH$ groups in the macroinimer[13]. The signals of $-CH_2$ and $-CH_3$ groups of PDMS can also be seen in *Figure 1*.

Figure 2 shows the i.r. transmittance of obtained MIM I. The characteristic peaks of macroinimer were observed at $3320\,cm^{-1}$ for the $-NH$ stretching vibration band, and at 1650 and $1540\,cm^{-1}$ for carbonyl absorption. The peaks at $1620\,cm^{-1}$ is due to C=C vibrations, at 1260 and $800\,cm^{-1}$ for $Si-CH_3$ deformation, and at $1024\,cm^{-1}$ for Si–O–Si assymmetric stretching vibration.

Thermal homopolymerization of MIM I was investigated at 60, 70 and 80°C. The results are collected in *Figures 3a–c*. MIM I homopolymerization in bulk was carried out using 0.3 g of MIM I in a pyrex tube at 80°C. After polymerization, the tube content was extracted with an excess amount of chloroform (see Experimental). The percentage of crosslinked polymer was calculated as a ratio of dry crosslinked polymer to the initial MIM I amount. The soluble part remaining in chloroform solution may contain various species such as unreacted macroinimer chains, linear polymer and also branched units. Since it is not practically possible to separate the soluble, linear polymer from the mixture, we mention

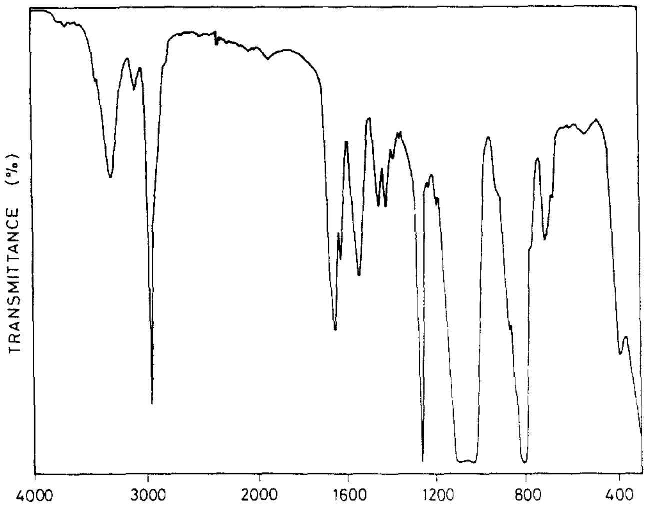

Figure 2 I.r. transmittance spectrum of the macroinimer (MIM I)

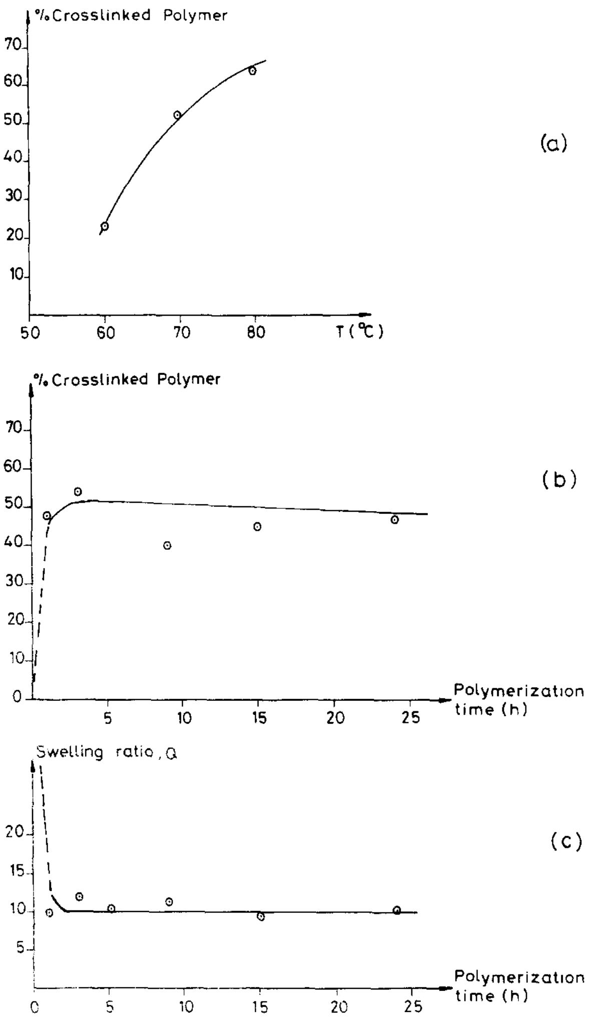

Figure 3 (a) Yield of crosslinked polymer vs temperature curve for homopolymerization of MIM I for 5 h. (b) Yield of crosslinked polymer vs polymerization time for the homopolymerization of MIM I at 80°C. (c) Swelling ratio vs polymerization time for crosslinked MIM I samples at 80°C

only the percentage of crosslinked polymer as the yield of crosslinking reaction for MIM I. The reaction seems to be completed in 1 h, no additional crosslinking reaction takes place after 1 h and the percentage of crosslinked polymer remains constant ($\approx 45\%$) as shown in *Figure 3b*. Also, the swelling ratio at equilibrium, Q, did not change after 1 h. The decrease in Q up to 1 h is expected from the conventional gelation theory, then it becomes constant ($Q = 10$) as can be seen in *Figure 3c*. However, it is important to note that, the yields of crosslinked polymer seem to be low in the MIM I homopolymerization reaction. A similar trend was also observed in the poly(tetrahydofuran) macroperoxyinimer system which was reported recently[14]. We suggest that there is a possibility for formation of some inactive species which terminate by disproportionation in the reaction of azo radicals and vinyl groups. These may lead to decreasing crosslinked polymer yield. In this connection, we might also say that chain transfer to PDMS blocks and/or the termination is more likely to occur in radical polymerization of macromonomers[15]. Additionally, the amount of azo group and polymerizable vinyl groups per macroinimer molecule decreases as the chain length between the two vinyl ends increases. The macroinimer, MIM I ($M_n \cong 2400\,\mathrm{g\,mol^{-1}}$), has ~ 1 wt% azo group and ~ 2 wt% vinyl groups.

Kinetics of low-conversion polymerization

MIM I was utilized as a free radical initiator for bulk polymerization of styrene at 60°C. Conversions were kept below 17 wt% for proper analysis of kinetic results. The results for bulk polymerization of styrene at 60°C are given in *Table 2*.

Specific viscosities of the samples were measured at 25°C in toluene. Intrinsic viscosities given in *Table 2*, generally decrease with increase in MIM I concentration. Molecular weights of the samples determined the g.p.c. technique, M_n and M_w values also decrease with increasing MIM I content in the samples. Polydispersity shows a variation between 1.82 and 3.02. In the radical polymerization, it is well known that R_p is given by the following relation[16–21].

$$R_p = k_p[M]\left(\frac{fk_d\,[I]}{k_t}\right)^{1/2} \tag{1}$$

by taking

$$K = k_p\left(\frac{fk_d}{k_t}\right)^{1/2} \tag{2}$$

where [I] and [M] are the initiator and monomer concentrations, k_d, k_p, and k_t are the thermal decomposition, propagation and termination rate constants, respectively, and f is called the initiator efficiency. The term $k_p(fk_d/k_t)^{1/2}$ is often denoted K and is a measure of the initiator reactivity.

The value of K^2, can be obtained from the slope of the plot of R_p vs $[M]^2$ [I] as can be seen from equation (2). For our system (styrene-MIM I), K was estimated from *Figure 4* as 1.15×10^{-4} which is comparable to that of a common initiator, AIBN = $3.88 \times 10^{-4}\ \mathrm{l^{1/2}\,mol^{-1/2}\,s}$ (ref. 22). For free radical polymerization, the average degree of polymerization (P_n) is related to the rate of polymerization (R_p) via the following equation[16,22].

$$1/P_n = C_M + \{k_t/k_p^2[M]^2\}R_p + \{C_I/K^2[M]^3\}R_p^2 \tag{3}$$

Here C_M and C_I represent the chain transfer constant to monomer and to initiator, respectively. For bulk polymerization, a plot of $1/P_n$ *versus* $R_p/[M]^2$ is shown in *Figure 5*. The intercept of this curve with the $1/P_n$ axis gives C_M which was found to be 0.30×10^{-4}. It is in agreement with the literature values of C_M for styrene[23]. The curvature leading to higher P_n observed at high $R_p/[M]^2$ values may result from the delaying termination reactions because of the high viscosity of the reaction media.

Crosslinking of styrene with MIM I at 80°C

Bulk polymerization of styrene with MIM I was also carried out at 80°C. MIM I concentration was kept constant (18 wt% in styrene mixture). The time vs conversion curve is shown in *Figure 6*. Up to 43 wt% yield (180 min), soluble polymers were obtained. Apparent M_n and M_w values were obtained from g.p.c. measurements. M_w and polydispersity of polymers show an increase with polymerization time. However, M_n values exhibit a tendency to remain constant. In this manner, branching occurs as the polymerization proceeds. After 240 min reaction time, crosslinked polymers were obtained. The results are given in *Table 3*.

The crosslinking reaction of styrene with MIM I was also carried out at 80°C, for 70 h with varying MIM I concentration. Crosslinked PDMS-b-PS block

Table 2 Bulk polymerization of styrene with macroinimer at 60°C

Run no.	MIM I (g)	Styrene (g)	MIM I (wt%)	$[I]_0$ [a] (mol l^{-1} $\times 10^3$)	$[M]_0$ [b] (mol l^{-1})	Time (min)	Yield (wt%)	R_p (mol l^{-1} s^{-1})	η [c] (dl g^{-1})	$M_v^{app.}$ (g mol^{-1} $\times 10^{-3}$)	$M_n^{app.}$ (g mol^{-1} $\times 10^{-3}$)	$M_w^{app.}$ (g mol^{-1} $\times 10^{-3}$)	P.D. [d]
1	0.0039	4.098	0.095	0.341	8.35	290	3.11	0.149	2.533	1091	758	1380	1.82
2	0.0084	4.054	0.21	0.742	8.34	255	4.11	0.224	1.713	648	281	844	3.00
3	0.0165	4.093	0.40	1.442	8.32	225	5.37	0.333	1.850	694	277	750	2.71
4	0.0261	4.085	0.63	2.279	8.30	195	5.49	0.392	1.476	531	280	670	2.39
5	0.0517	4.088	1.25	4.483	8.25	165	5.93	0.500	1.166	388	168	464	2.76
6	0.0592	2.211	2.61	9.358	8.14	135	8.91	0.919	0.613	165	108	311	2.88
7	0.2562	2.218	10.3	37.17	7.49	90	16.7	2.57	0.295	62	49	148	3.02

[a] $[I]_0$ = Initial MIM I concentrationin mol l^{-1}
[b] $[M]_0$ = Initial styrene concentration in mol l^{-1}
[c] $[\eta] = 7.5 \times 10^{-5}\ M_v^{0.75}$ (25°C, tolulene, ref. 20)
[d] P.D.: Polydispersity
app: Apparent values

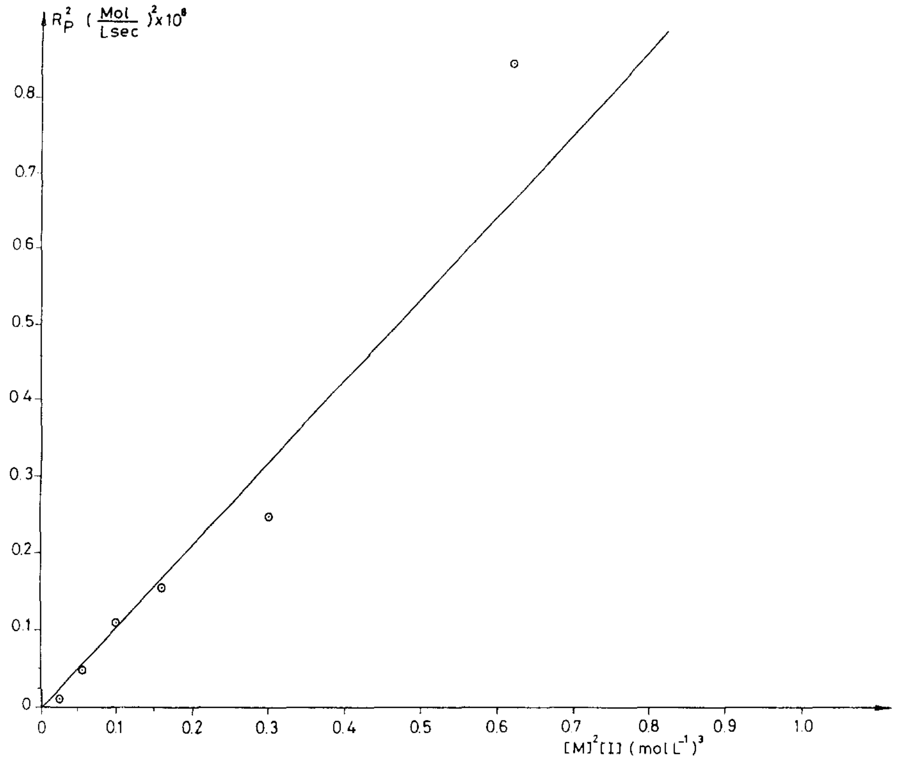

Figure 4 Plot of R_p^2 vs $[M]^2$ [I] for styrene polymerization in bulk at 60°C, initiated by MIM I

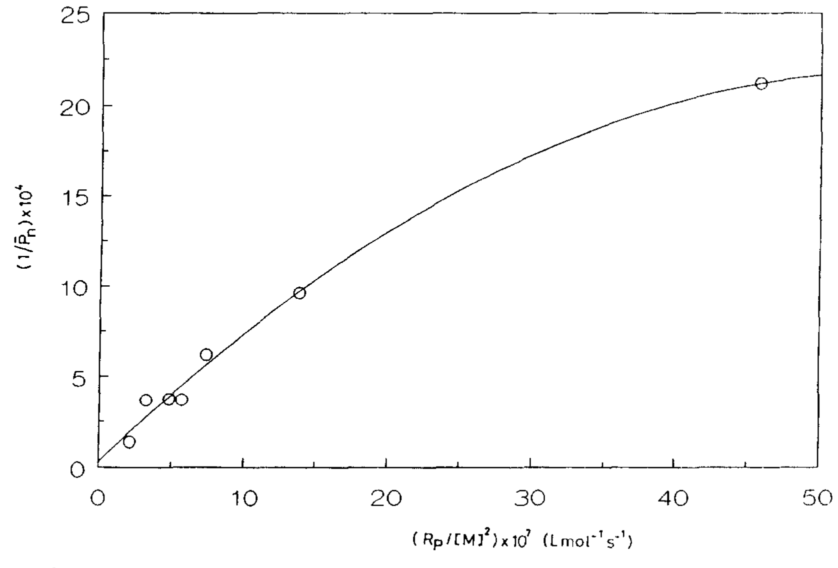

Figure 5 Plot of $1/P_n$ vs $R_p/[M]^2$ for styrene polymerization at 60°C initiated by MIM I

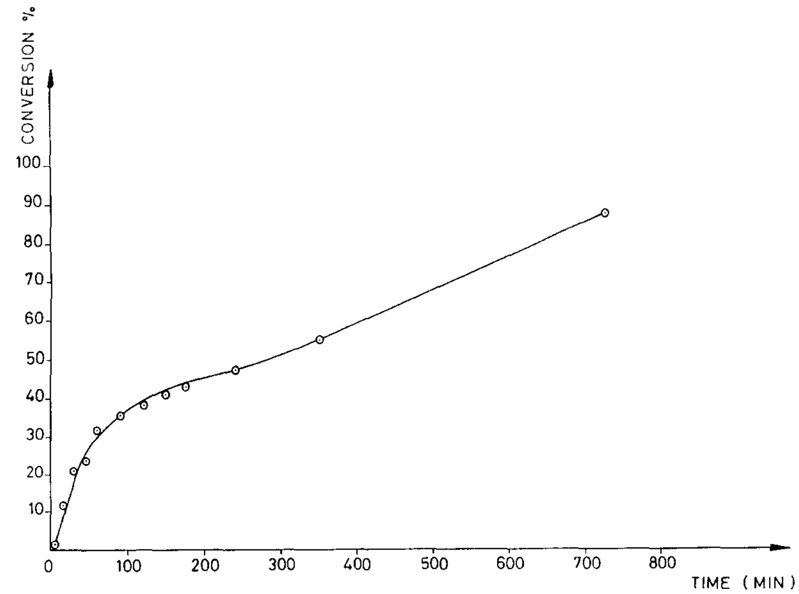

Figure 6 Time vs conversion curve for polymerization of styrene with MIM I at 80°C (constant MIM concentration 18 wt%)

Table 3 Bulk polymerization and crosslinking of styrene with macroinimer at 80°C (constant MIM concentration)

Run no.	MIM I g	MIM I mol $\times 10^4$	Styrene g	Styrene mol	MIM I (wt%)	(min)	Yield wt% Crosslinked polymer	Yield wt% Soluble part	$M_n^{app.}$ ($g\,mol^{-1}$ $\times 10^{-3}$)	$M_w^{app.}$ ($g\,mol^{-1}$ $\times 10^{-3}$)	P.D.
8	0.498	2.054	2.280	0.022	17.9	5	—	2.57	28.5	51.1	1.79
9	0.505	2.083	2.325	0.022	17.8	15	—	11.5	30.5	63.9	2.09
10	0.504	2.079	2.236	0.021	18.4	30	—	21.1	28.2	85.7	2.68
11	0.499	2.058	2.265	0.022	18.0	45	—	24.0	30.2	88.7	2.93
12	0.490	2.021	2.386	0.023	17.3	60	—	31.7	28.9	113	3.91
13	0.251	1.028	1.094	0.010	18.7	90	—	35.9	33.9	151	4.45
14	0.259	1.068	1.091	0.010	19.1	120	—	38.5	33.6	152	4.52
15	0.253	1.044	1.095	0.010	18.8	150	—	41.2	26.0	157	6.03
16	0.256	1.056	1.118	0.011	18.7	180	—	43.3	25.3	153	6.05
17	0.128	0.528	0.541	0.005	19.2	240	44.3	2.7	—	—	—
18	0.127	0.524	0.552	0.005	18.8	350	52.1	2.9	—	—	—
19	0.228	0.940	0.913	0.008	19.9	720	86.9	—	—	—	—

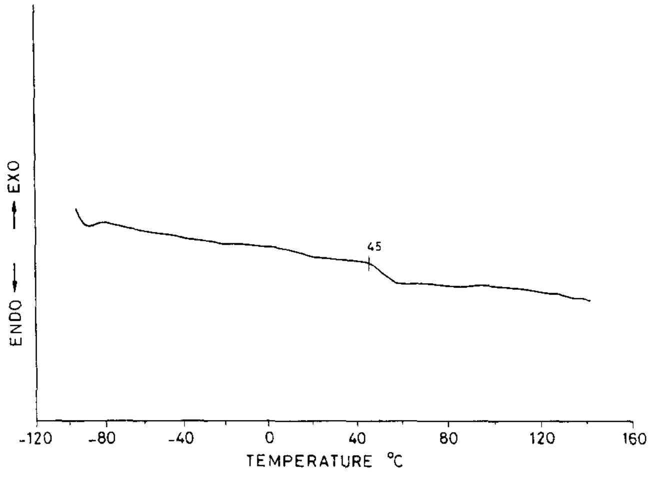

Figure 7 D.s.c. thermogram of crosslinked PDMS-b-PS copolymer (run no. 25, *Table 4*)

copolymers were produced. The results are shown in *Table 4*. The yields of crosslinked polymers are high except the sample in Run No. 20 with the lowest MIM I concentration, 0.815 wt%. Swelling ratios of the crosslinked polymer samples were determined by gravimetry in chloroform at 25°C. The swelling ratio, Q value, is approximately 7.0 for all samples of crosslinked PDMS-b-PS block copolymers and 10 for homonetwork. The lower swelling ratio of the crosslinked copolymers may be explained by the lower content of rubbery component (10 wt% of PDMS) in the copolymer with respect to higher PDMS content in MIM I homonetwork (60 wt% of PDMS).

The glass transition temperatures (T_gs) of crosslinked PDMS-b-PS copolymers were determined by d.s.c. measurements. Only one T_g could be observed at around 45°C for all crosslinked samples in the temperature range (−100 to 150°C). This is evidence for a

Table 4 Crosslinking reaction of styrene with macroinimer (MIM I) at 80°C for 70 h

	MIM I		Styrene			Yield wt%		
Run no.	g	mmol $\times 10^5$	g	mmol	MM I (wt%)	crosslinked	soluble	Swelling ratio, Q
20	0.059	2.434	7.181	0.0689	0.815	63.0	9.6	—
21	0.145	5.982	7.237	0.0695	1.96	98.6	1.4	8.0
22	0.248	10.58	7.173	0.0689	3.34	97.5	2.5	9.5
23	0.436	18.60	7.230	0.0694	5.69	100	—	6.4
24	1.035	44.15	7.210	0.0692	12.55	100	—	7.0
25	1.512	64.50	7.245	0.0696	17.27	100	—	5.3

plasticizing effect of flexible PDMS segments depending on the wt% of PDMS in the copolymeric samples. It is important to note that this kind of effect was also observed in the PDMS-b-PS block copolymers obtained with a macro-azo-initiator of PDMS in our previous work[9]. However, the T_g was around 88–91°C for this system. In the present work, PDMS macroinimer used in crosslinking reaction of PS causes T_g to move to lower temperatures. It can be said that crosslinking with this type of PDMS macroinimer may be an effective way to combine soft segments of siloxane with glassy polymer, polystyrene.

Figure 7 illustrates the d.s.c. thermogram of crosslinked polymer (run no. 25, *Table 4*) with 17.27 wt% MIM I content as representative.

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