Block Copolymers via Thermal Polymeric Iniferters. Synthesis of Silicone–Vinyl Block Copolymers

C. P. Reghunadhan Nair† and G. Clouet*

Institut Charles Sadron (CRM-EAHP), 6 rue Boussingault, 67083 Strasbourg, Cedex, France. *Received April 18, 1989; Revised Manuscript Received June 27, 1989*

ABSTRACT: Thermal polymeric iniferters (PI) based on poly(dimethylsiloxane) (PDMS) bearing thiuram disulfide groups along the chain were synthesized and characterized. For this (secondary amine) α,ω-bis-terminated PDMS were synthesized by the hydrosilylation reaction of silyl hydride terminated PDMS with allyl-*N*-methylamine. The macrodiamines of different molecular weights were transformed to the poly(thiuram disulfides) (or polymeric iniferter) by the thiocarbamylation reaction and oxidative coupling. The polymeric iniferters containing varying prepolymer segment lengths were characterized by viscometric, elemental, spectral, and differential scanning calorimetric analyses. The self-dissociation as well as the induced thermal dissociation of the PI was studied from the intrinsic viscosity variation with time. Polymerization of methyl methacrylate (MMA), styrene (ST), and acrylamide in presence of the PIs led to formation of multiblock copolymers containing PDMS and poly(MMA), polystyrene, or polyacrylamide segments and whose structures and compositions depended upon the PI structure, the monomer–PI ratio, and the extent of monomer conversion. Multiblock copolymers with a relatively larger number of alternating blocks and higher PDMS content were formed more easily in the case of styrene than in the case of MMA under identical conditions. Kinetics of polymerization studied in the case of MMA revealed that the polymeric iniferters are as efficient as their microanalogues from the point of view of their initiating and chain-terminating properties. DSC analyses of the block copolymers showed demixing of the siloxane blocks with the vinyl blocks when the siloxane chain length was more than 2000. When acrylamide was used as a monomer, amphiphilic block copolymers with different solubility characteristics were obtained.

Introduction

Polysiloxanes are characterized by certain salient features like thermooxidative stability, low-temperature processability, water repellancy, high gas permeability, impact resistance, etc. However, they possess poor mechanical properties, which limits their applicability. Incorporation of polysiloxane into conventional vinyl copolymers to form the block copolymers has been considered to bring about drastic improvements in the above-mentioned properties of the latter. There exist several preparative methods for silicone–vinyl block copolymers. Anionic living polymerizations of cyclic siloxanes and vinyl monomers are the prominent ones among them.[1-5] But the method is limited to anionically polymerizable monomers. Another method is based on the Pt-catalyzed polycondensation of α,ω-SiH-terminated PDMS with α,ω-divinyl-terminated vinyl polymers.[6] A generalization of this technique has led to the synthesis of a series of block copolymers of PDMS with various blocks of addition or condensation type.[7-9] Some free-radical methods have recently been introduced for the synthesis of PDMS–vinyl block copolymers. Crivello reported the use of bis(silyl pinacolate)-incorporated PDMS as macroinitiators for the polymerization vinyl monomers leading to their multiblock copolymers with PDMS.[10] Inoue made use of poly(azo-containing siloxaneamides) to effect similar synthesis.[11,12] The block copolymers reported by Crivello contain easily hydrolyzable Si–O–C bonds in the polymer backbone, which may lead to easy chain degradation in humid conditions. Inoue's method is limited to the formation of only triblocks in the case of monomers like MMA, which terminate mostly by disproportionation.

We have recently demonstrated applicability of the thermal initiator–chain transfer–terminator (iniferter) properties of the alkylthiuram disulfides to the perfect α,ω-difunctionalization of vinyl monomers by polymerization of the latter using the required functional thermal iniferter.[13,14] An extension of the technique led to the synthesis of thiuram disulfide containing poly(phosphonamides) as polymeric iniferters for the polymerization of vinyl monomers giving rise to phosphonamide–vinyl block copolymers.[15] In this paper we describe the synthesis of thiuram disulfide containing PDMS-based polymeric iniferters (PI) and their applicability for the synthesis of siloxane–vinyl multiblock copolymers. This paper describes the synthesis and the characterization of the PIs of different siloxane chain lengths and molecular weights. The synthesis and characterization of the block copolymers of PDMS with MMA, styrene, and acrylamide having different compositions are discussed along with a brief kinetic study in the case of MMA.

Experimental Part

Materials. The monomers methyl methacrylate (MMA) and styrene were purified by vacuum distillation from CaH_2 while acrylamide was recrystallized from THF. SiH-terminated PDMS was supplied by Rhône-Poulenc while allyl-*N*-methylamine was supplied by Fluka. CS_2, I_2, and H_2PtCl_6 (Aldrich) was used as received. Toluene, $HCCl_3$, triethylamine, and THF were distilled from CaH_2.

Instruments. ^{13}C and ^1H NMR spectra were recorded using Bruker 50- and 60-MHz NMR spectrometers, respectively. IR spectra were recorded on a Perkin-Elmer 983 spectrometer. DSC analyses were carried out using a Perkin-Elmer DSC II coupled with a thermal analysis data station at a heating rate of 20 °C/min. Viscosity measurements were done on a capillary type viscometer. Molecular weights were determined by a Shimadzu GPC calibrated using polystyrene and PMMA standards and THF as eluent. The detection was done by refractive index while the elution volume rate was maintained at 1 mL/min. Vapor pressure osmometry (VPO) measurements were carried out on a Knauer VPO in toluene using low molecular weight PDMS as standards.

Synthesis of α,ω-Bis[(*N*-methylamino)propyl]poly(dimethylsiloxane). In a typical experiment, 15 g of SiH-termi-

* Author to whom correspondence should be addressed.
† Permanent address: Polymer and Special Chemicals Division, Vikram Sarabhai Space Centre, Trivandrum 695022, India.

0024-9297/90/2223-1361$02.50/0

nated PDMS ($\bar{M}_n$ = 3050) was mixed under argon with 1.5 mL of allyl-*N*-methylamine containing 15 mg of H_2PtCl_6 dissolved in it. The system was heated slowly with agitation to 90 °C over a period of 90 min, and then the temperature was increased to 120 °C during another 1 h and maintained at this temperature for about 12 h. The excess amine was removed under vacuum at this temperature. The resulting product was freed of the catalyst by dissolving it in heptane and water washing. The solution after drying over Na_2SO_4 was freed of the heptane under vacuum. It was characterized by end-group analysis, NMR, and viscometry. The other diamines were synthesized exactly under similar conditions.

Synthesis of Polymeric Iniferter. The above diamine (14 g) was dissolved in 50 mL of $CHCl_3$. To this were added 2 mL of triethylamine and 0.7 g of CS_2. The system was allowed to react for about 1 h at room temperature. A solution of I_2 in $CHCl_3$ was then added dropwise under agitation until the violet color of I_2 persisted. Toward the end, the iodine addition was done very slowly. The $CHCl_3$ solution was washed with water and then dried over Na_2SO_4 for at least 1 day. The $CHCl_3$ was evaporated off under reduced pressure at room temperature. Quantitative yield of a brown greasy product was obtained. Characterization was done by elemental and spectral analyses and viscometry.

Alternatively, the synthesis could be effected in heptane solution, in which case the triethylamine hydroiodide formed precipitated and was removed by filtration. The heptane was evaporated off to get the polymeric iniferter, which was kept in the cold and in the dark until use.

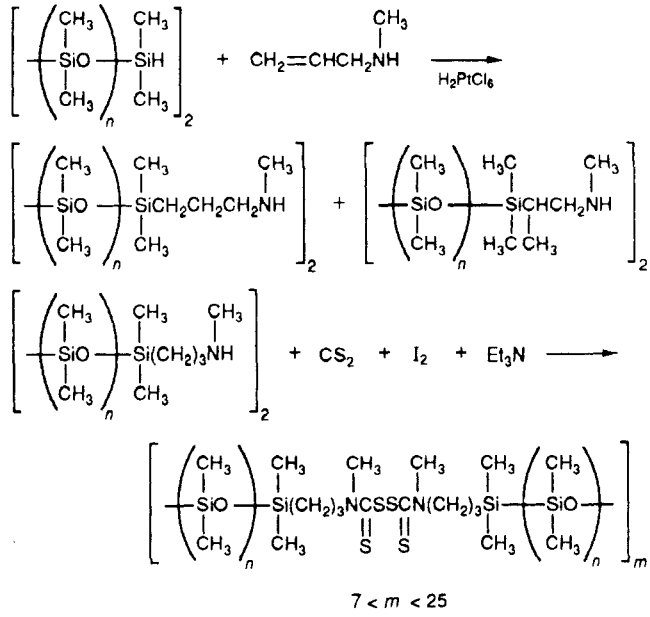
Polymerization. The polymerization was effected in sealed evacuated glass tubes. The tube containing the monomer and the PI was deaerated by several cycles of freezing and thawing and then sealed under vacuum (1 mm). The polymerization was done in electrically controlled thermostates. After the polymerization, the contents was dissolved in THF and precipitated into methanol. The unreacted PI was removed by thorough extraction with petroleum ether in the cold. The polymers were dried under vacuum at 40 °C. They were characterized by elemental analysis for Si and by GPC for molecular weight. For kinetic studies, the conversions were limited to less than 7%. In such cases, the polymer precipitated in MeOH was collected on a sintered-glass crucible, dried, and weighed. The rate of polymerization was determined from the time–conversion plots.

For acrylamide, the polymerization was done in THF. The copolymer formed, precipitated in the medium, which was filtered, washed with THF, and dried. The block copolymers were characterized for the overall composition by the analysis for Si.

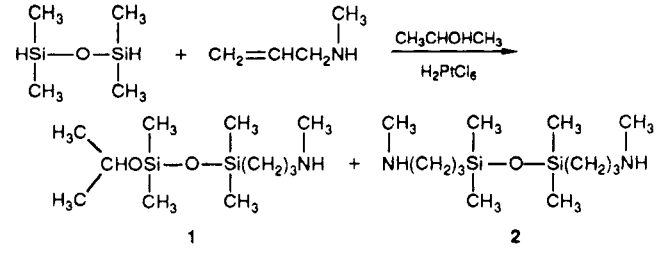
Results and Discussion

Since thiuram disulfides are known to behave as initiators, chain-transfer agents, and polymer radical terminators during thermal vinyl polymerization; all the polymer chains formed in their presence are invariably end-capped with their fragments. Hence, when they are incorporated in a polymeric backbone, polymerization of vinyl monomers in their presence should be expected to lead to multiblock copolymers by extension of the principle of iniferters. This special feature of the thiuram sulfide moiety has already been exploited by us for the synthesis of phosphonamide block copolymers with MMA and styrene. In the present study, we wanted to extend this technique to the synthesis of siloxane–vinyl block copolymer. This necessitated the synthesis of PDMS bearing thiuram disulfide groups in their backbone for use as thermal iniferter for the polymerization of vinyl monomer.

Synthesis and Characterization of PDMS-Based PI. (Secondary amine) α,ω-bis-terminated PDMS's were synthesized by the hydrosilylation reaction using SiH-terminated PDMS and allyl-*N*-methylamine. Subsequent chain extension of the macrodiamine by the thiocarbamylation reaction using CS_2 and oxidative coupling using I_2 led to the formation of the polymeric iniferters. The overall reaction scheme can be depicted as follows:



The hydrosilylation reaction is widely applied to the synthesis of α,ω-bifunctional polysiloxanes for further polymer modifications.[16,17] Side reactions involving the silyl hydride groups and other inadvertently present impurities are frequent in this reaction. Normally, the catalyst for the reaction H_2PtCl_6 is employed as an alcoholic solution (isopropyl alcohol or *tert*-butyl alcohol). In this case part of the SiH groups reacts with alcohols to give nonfunctional chain ends, thereby leading to a decrease in the end functionality of the modified PDMS.[6,17] We also found that when isopropyl alcohol is used as a solvent for H_2PtCl_6 in the presence of the allylamine, a large proportion of the SiH bonds reacts with the alcohol. In this particular case, the hydrosilylation reaction with allyl-*N*-methylamine was found to be very slow. Very high temperatures (120 °C) and prolonged reaction times (10–12 h) were required for the complete reaction of the SiH bonds. Under these circumstances, competitive side reactions are probable. In a model reaction using tetramethyldisiloxane and allyl-*N*-methylamine in the presence of an isopropyl alcohol solution of H_2PtCl_6 and subsequent isolation of the product by fractional distillation, about 35% of the product isolated corresponded to the one where isopropyl alcohol had reacted at one end and allylamine on the other. The ^1H NMR of this product (1) (mixture of isomers) is given in Figure 1 with the assignments:



However, when polymers were employed, the extent of side reactions could be minimized in consistency with the observation of others. It was found that H_2PtCl_6 forms a clear solution in allyl-*N*-methylamine. Hence, this solution was directly employed for the synthesis. The progress

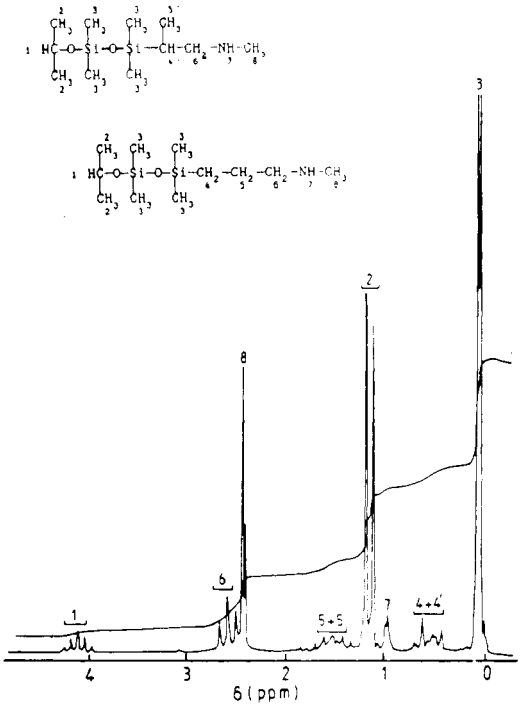
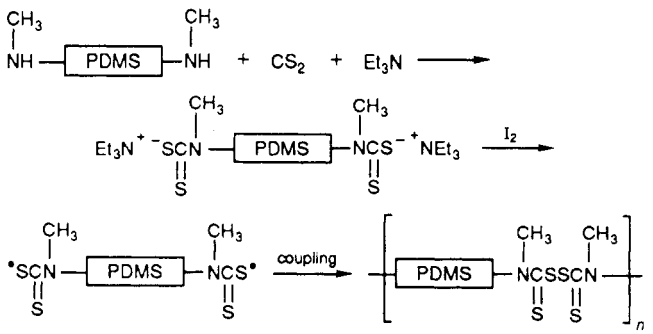


Figure 1. ^1H NMR ($CDCl_3$) of the isopropyl alcohol adduct of the hydrosilylation reaction.

of the reaction was followed by monitoring the disappearance of the IR absorption at 2135 cm^{-1}, due to the SiH bond. The macrodiamines, when characterized by end-group analysis and molecular weight, revealed an augmentation in molecular weight during the hydrosilylation reaction. This has arisen from the partial hydrolysis of SiH bonds by the inadvertently present water in PDMS and subsequent condensation of SiOH bonds. (Since this side reaction was not detrimental to the functionality of the polymers, no attempts were made to perfectly dry the reaction medium).

A good agreement between the end-group analysis and the molecular weight confirmed the bifunctionality of the resulting polymer. Analytical data pointed out to the absence of any reaction involving SiH and NH groups. When the diamines were characterized by ^{13}C NMR spectroscopy, evidences were obtained for the hydrosilylation reactions taking place both in the anti-Markovnikov and the Markovnikov manner. The Markovnikov adduct amounted to 58% for PDMS having molecular weight 400 and 40% for the rest as estimated from the ^{13}C NMR spectra. A typical ^{13}C NMR spectrum can be seen in Figure 2 for one such diamine.

The chain extension of the diamines was carried out by reaction with CS_2 and I_2. The mechanism of chain growth involves coupling of the bis(dithiocarbamyl) radicals as follows:



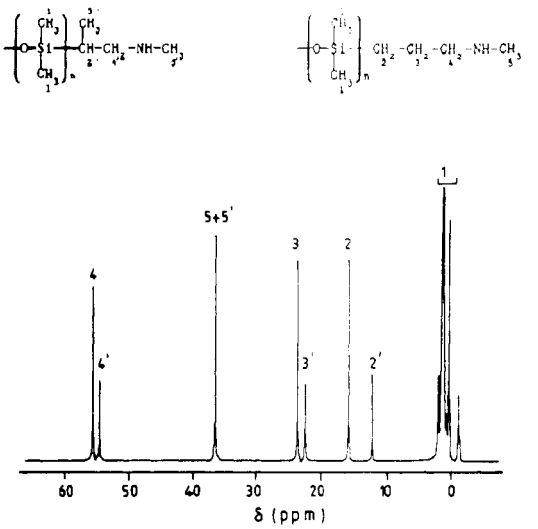


Figure 2. ^{13}C NMR ($CDCl_3$) of the amino-terminated PDMS (molecular weight 1550).

By this reaction, which is a radical chain extension reaction, high molecular weight poly(thiuram disulfides) having the "degree of chain extensions" up to 25 were formed. As in a step reaction, the $\overline{DP}$ would be dependent on the functionality of the diamines and the extent of reaction. The reaction of amines is quantitative, as evidenced from the amount of I_2 consumed and the proportion of N and S in the isolated product. The characteristics of the diamines and their PIs are given in Table I. The polymeric iniferters were characterized by elemental analyses (Table II) and NMR (^{13}C and ^1H). Figure 3 shows a typical ^{13}C NMR spectrum of a poly(thiuram disulfide). It is interesting to note the complete downward shift of all C–N signals in the disulfide. $N-CH_3$ groups in the two isomers can be well distinguished in the ^{13}C NMR of their thiuram disulfides. The molecular weights were determined by VPO for the oligomer designated as PI_1 and its prepolymers and from intrinsic viscosity for the rest using toluene as solvent. The literature values of K and a of PDMS were chosen for the molecular weight calculation from $[\eta]$ under the assumption that the small amount of thiuram disulfide groups does not alter them significantly. The relationship used is $[\eta] = 21.5 \times 10^{-5}M^{0.65}$ dL/g (in toluene at 25 °C; in this equation M corresponds to the molecular weight determined by osmometry[18]).

In this study, three types of Si–H PDMS compounds of $\bar{M}_n$ = 400, 1070, and 3050 were used. Table I lists the details regarding the characteristics of the diamines and their poly(thiuram disulfides). Since the polymer chain buildup by the chain-extension reaction will be limited by the presence of monofunctional PDMS, by the relative proportion of the amine and CS_2 concentration (amine in excess), and by the extent of reaction, this reaction in a sense resembles a step-growth polymerization between the diamine and CS_2. Hence, the molecular weights of PI should be sensitive to the variation in the functionalities of the prepolymers. As there may be inevitable error in the functionality determination from the molecular weight by viscometry and end-group analyses, no attempt was made to quantitatively correlate the PI molecular weight and the amine functionality of this "step-growth" type reaction. The bifunctionality was indirectly evident from the high molecular weight of the coupled polymers. The step-growth nature of the coupling reaction was exemplified in a typical experiment where the molecular weight of the PI was followed as a function of the

Table I
Characteristics of the Prepolymers and Polymeric Iniferters

$\bar{M}_n$ of Si-H-terminated PDMS	$\bar{M}_n$ after hydrosilylation	NH, %	functionality	$\bar{M}_n$ of polymeric iniferter	degree of chain extension	ref for the polymeric iniferter
400	625[a]	5.10	2.12	4400[a]	5.7	PI_1
1090	1550	1.74	1.82	44200	26.0	PI_2
3050	4500	0.55	1.65	101000	22.0	PI_3
3050	4690	0.62	1.92	61000	12.6	PI_4

[a] By VPO.

Table II
Elemental Analysis of the Poly(thiuram disulfides)

	C		H		N		S		Si	
mol wt of the macrodiamine	calc	found	calc	found	calc	found	calc	found	calc	found
625	35.95	36.81	7.47	7.62	3.52	3.63	16.10	15.63	25.14	24.19
1550	33.90	34.25	7.77	7.90	1.65	1.62	7.52	7.69	31.30	30.61
4500	32.96	33.06	7.98	8.07	0.64	0.53	2.75	2.92	35.40	34.98

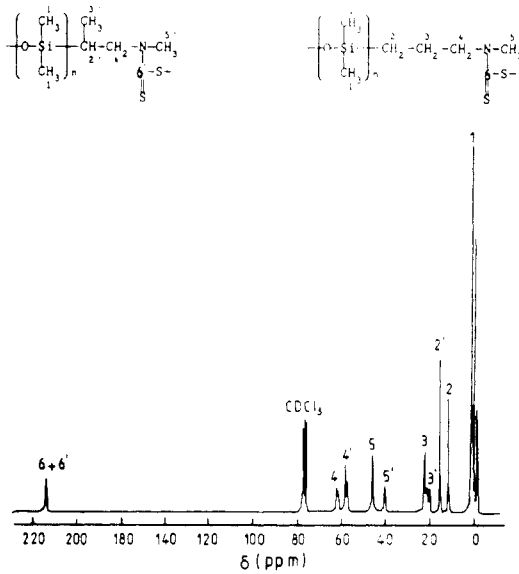


Figure 3. ^{13}C NMR ($CDCl_3$) of the poly(thiuram disulfide) (PI_1).

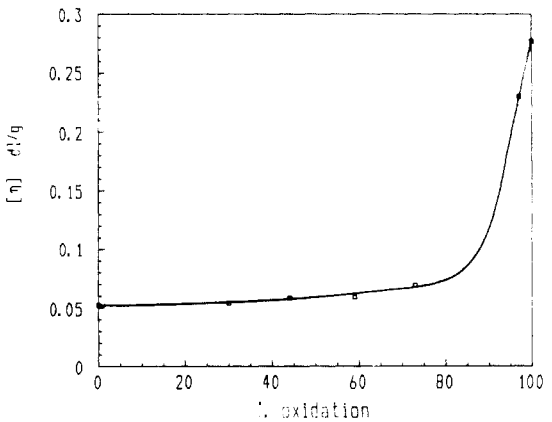


Figure 4. Variation of molecular weight as a function of the extent of oxidation for PI_3.

extent of oxidative coupling by regulating the concentration of the oxidizing agent (I_2). Figure 4 shows the evolution of molecular weight in this case. It was found that, initially, the increase in molecular weight is very insignificant and, toward the end of the reaction, the increase was tremendous, resembling the case of a step reaction.

As in any step reaction, the molecular weight of the PI can be controlled either by the extent of oxidation or by the addition of calculated amounts of monofunctional compounds (secondary amines). Alternately, this can be realized by decreasing the concentration of CS_2 in the reaction system. The elemental analysis for the PI cited in Table II, shows a good consistency between the observed and theoretical ones for a given prepolymer molecular weight. An excellent rapport between N and S contents rules out the possibility for any nucleophilic reaction between the SiH and the Amine, as may normally be anticipated.

Solubility and Thermal Characteristics of the PI. The PI had similar characteristics as PDMS, except for the shorter siloxane chain lengths (PI_1 SCL 625) where insolubility in heptane resulted, due to the large proportion of the thiuram disulfide groups. Thermogravimetric analysis showed a weight loss between 160 and 210 °C due to the decomposition and eventual evolution of CS_2. DSC showed an exotherm between 160 and 210 °C corresponding to this reaction of the thiuram disulfide groups. The activation energy for the thermal decomposition, calculated by the method of Rogers[19] corresponded to 640 kJ/mol (of thiuram disulfide). The T_gs of the PI of different SCL did not show any marked trend with composition. Weak exotherms due to crystallization were to be seen in their DSC for these PI (PI_1 and PI_2, 172 K; PI_3, 210 K). In SCL 4700 (PI_3), a single endotherm was observed at 230 K, whereas for SCL 1550 (PI_2) and 625 (PI_1) three very prominent endotherms probably corresponding to fusion of the specific crystallites were to be seen at 191, 199, and 202 K, respectively. The crystallization at lower temperature in short SCL-PI might be aided by the specific interaction between the thiuram disulfide groups. Similar strong physical interactions are known to exist between C=S groups in poly(carbon disulfide). In short SCL-PIs (PI_1 and PI_2), the glass transitions were ill-defined. Figure 5 shows typical DSC thermograms of the PIs. It is noteworthy that PI_2 and PI_3 have high molecular weights. Despite that, the difference in temperatures for the various physical phenomena shows that they are functions of the flexible segments between the thiuram disulfide groups and not the entire molecule.

Since the thiuram disulfides can undergo thermal scission, it was of interest to study the change in molecular weight of the polymeric iniferters by thermal aging. When the thermal decomposition was performed in the solid state at 90 °C, it was found that the change in molecular weight was not very significant, whereas in toluene solution the decomposition was much more rapid as can be seen in Figure 6. It may be that, in the solid state, due to the limited translational degree of freedom and the absence of a third body, the macroradicals produced

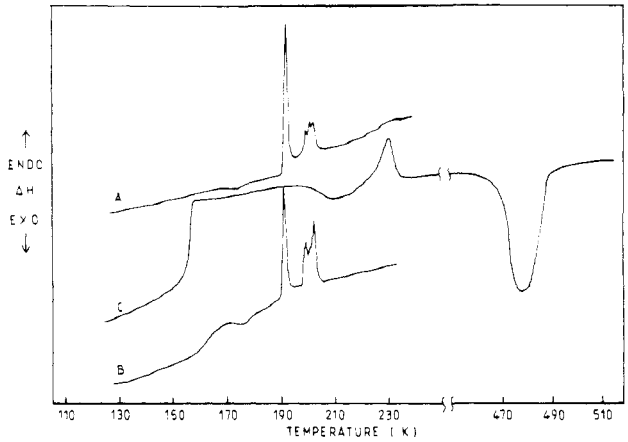


Figure 5. DSC thermograms: A, PI_1; B, PI_2; C, PI_3. Heating rate 20 °C/min.

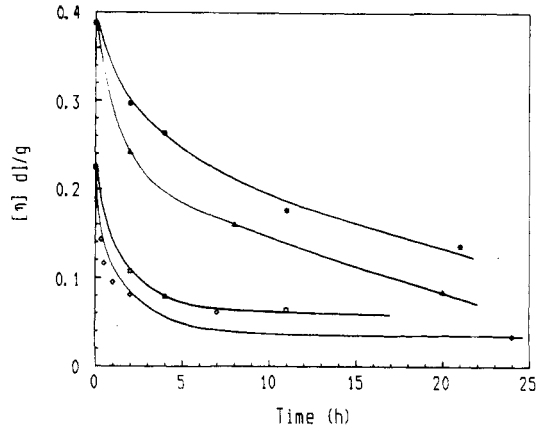


Figure 6. Thermal degradation in toluene solution: *, PI_4; △, PI_4 + 0.5% AIBN; □, PI_2; ◇, PI_2 + 0.5% AIBN.

are not easily scavenged and are terminated to a great extent by recombination. At 90 °C, the thiuramyl radicals do not lose CS_2. In toluene solution, secondary reaction of the macroradicals leading to the easy chain degradation is possible. The chain degradation was much more rapid when a free-radical source was introduced by the decomposition of AIBN. Figure 6 also illustrates this. In this case, the primary radicals either can undergo chain-transfer reaction with the macroiniferter at the S–S linkage or can couple with the macroradicals, in either case, causing an easy chain degradation. This observation further substantiates the proposed mechanism of block copolymer formations by chain transfer and radical cross-coupling when PI is used to initiate a vinyl polymerization.

$$\text{AIBN} \rightarrow \text{R}^\bullet$$

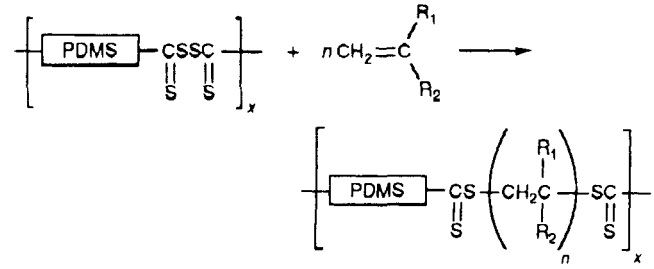
$$\text{R}^\bullet + [\text{PSS}-]_n \rightarrow [\text{PS}\dagger_x\text{R} + [\text{PS}^\bullet]_y \qquad x + y = n$$

$$\text{R}^\bullet + [\text{PS}^\bullet]_y \rightarrow [\text{PS}\dagger_y\text{R}$$

The thermal degradation of the PI to the "monomers" was nearly complete in 24 h at 90 °C.

Block Copolymer Synthesis. Since the thiuram disulfide groups carried on the polysiloxane backbone can act at the same time as initiators, chain-transfer agents, and polymer radical terminators, polymerization of vinyl monomers in their presence should lead to perfect multiblock copolymers. The reaction scheme for the block copolymer formation can be depicted as follows in an ideal case:

One can envisage the polymer growth as an insertion of the vinyl block across the disulfide linkage between



two PDMS blocks. Evidently in such a synthesis, the vinyl block length and the number of blocks would be a function of the PI concentration, its composition, and the extent of monomer conversion. In this study, block copolymers of MMA and styrene with PDMS were synthesized by the bulk polymerization of the vinyl monomer with the required PI. But for acrylamide, the copolymerization was effected in THF and the polymer precipitated in the medium was isolated by filtration. The copolymers of MMA and styrene were prepared using the PI_2, PI_3, and PI_4 at different concentrations and monomer conversions. In each case, the polymers were first precipitated in MeOH and then purified by repeated extraction with petroleum ether at room temperature. The Soxhlet extraction was avoided since the hot solvent is known to dissolve out the polymers richer in polysiloxane. The compositions of the copolymers were determined from the silicon content and molecular weights.

Kinetics of Polymerization of MMA. The kinetics of polymerization of MMA using iniferters and polymeric iniferters has been extensively carried out.[13-15] In previous studies, the iniferter properties were well demonstrated. In this study, with a view to understand the initiating efficiency, as well as the extent of primary radical termination, which contributes to the mechanism of block copolymer formation, the kinetics of polymerization of MMA was carried out at 70 °C, using PI_3. The rates of polymerization (R_p), determined gravimetrically as a function of the iniferter concentration, are quoted in Table III. The kinetic expression relating the R_p and the [PI] in a limited concentration range, is of the form[15]

$$R_p^2 = \frac{R_{p0}^2 + A^*{}^2[\text{PI}]}{1 + 2B^*[\text{PI}]/[\text{M}]} \qquad (1)$$

where R_{p0} is the rate of thermal polymerization in the absence of catalyst and A* and B* are complex constants, which are measures of the initiating, as well as the polymer radical terminating capacities of the PI as described elsewhere.[13] Using a computer program A* and B* of eq 1 were resolved using the experimental data in Table III. Figure 7 shows the R_p^2 vs [PI] plot using these constants. Within experimental limits, the experimental points conform to the theoretical curve. As the PI concentration increases, a retardation effect can be seen which is due to the participation of the thiuramyl radicals in termination reactions coupled with the degradative chain transfer to the iniferter. Table III enlists the kinetic constants pertaining to the polymerization of MMA under these conditions. The overall thermal dissociation constant ($2fk_d$) calculated from A* shows that they are comparable to those of simple iniferters.

Block Copolymer Synthesis at Fixed PI Concentration. The block copolymers were synthesized using PI_2 and PI_3 (or PI_4) at fixed concentration for the polymerization of MMA and styrene to different conversion levels. The details are given in Tables IV and V. Knowledge of the global composition and the molecular weight

Table III
Rate of Polymerization and Kinetic Constants at 70 °C

[PI] × 10^4,[a] mol·L^{-1}	1.21, 2.42, 4.85, 9.71, 18.20, 36.41
$R_p \times 10^5$, mol·L^{-1}·s^{-1}	1.88, 2.39, 4.18, 5.6, 6.27, 7.1
A^*, $L^{-1/2}$·$mol^{1/2}$·s^{-1}	2.114×10^{-3}
$2fd_d$, s^{-1}	2.174×10^{-6}
B^*	2729

[a] Expressed in terms of the molar concentration of the thiuram disulfide groups.

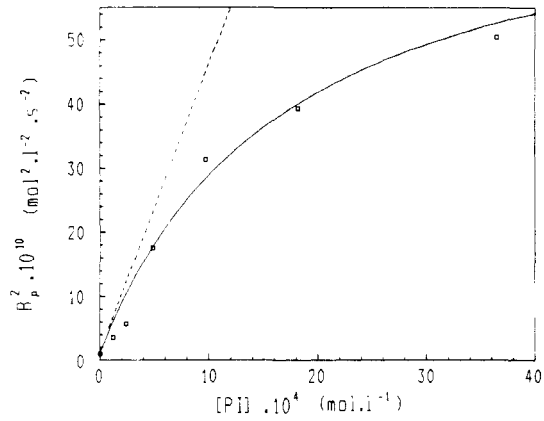


Figure 7. Dependence of R_p on [PI]: (—) regression curve, (□) experimental points, (- -) theoretical prediction for a normal initiation.

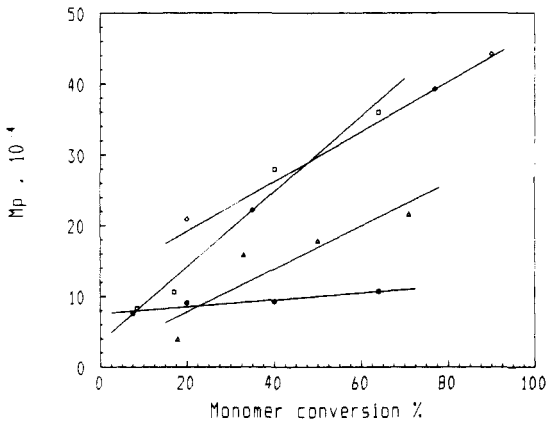


Figure 8. Evolution of molecular weight ($\bar{M}_p$) of the block copolymers with monomer conversion: *, MMA–PI_2; △, styrene–PI_2; □, MMA–PI_3; ◇, styrene–PI_4.

permitted calculation of the number of A–B sequences. For this $\bar{M}_p$ values (mass corresponding to the maximum in the GPC) were adopted, since they represent the true molecular weight in narrow distributed polymers. It was found that the molecular weight of the polymers increased with an increase in monomer conversion with a concomitant decrease in silicone content. The variations of molecular weight with conversion in monomer are illustrated in Figure 8. This substantiates the mechanism of polymer growth by the successive insertion of the vinyl block across the disulfide linkage. This behavior is similar to the one reported for the synthesis of block copolymers using aromatic polysulfides as polymeric chain-transfer agents.[21] Since the copolymers prepared at lower conversions contain active disulfide groups (as evidenced from the DSC analysis), they were aged in toluene at 90 °C for 3 days in order to dissociate any residual disulfide group. It was found that, in most of the cases, considerable changes in molecular weight and their distribution were observed (refer to Tables IV and V). Figure 9 shows the representative GPC curves in such a case. It can be seen from Tables IV and V that the average block numbers increase slightly with conversion. For calculation of the average block number in the aged polymer in a series, the vinyl block length of the copolymer obtained at the highest conversion was adopted not withstanding the error involved in assuming that the vinyl block length does not change during the course of polymerization. The assumption has been made only to demonstrate the evolution of the block structure during the course of polymerization. It has further been observed that the silicone content in high conversion polymer does not decrease significantly after aging. The average vinyl

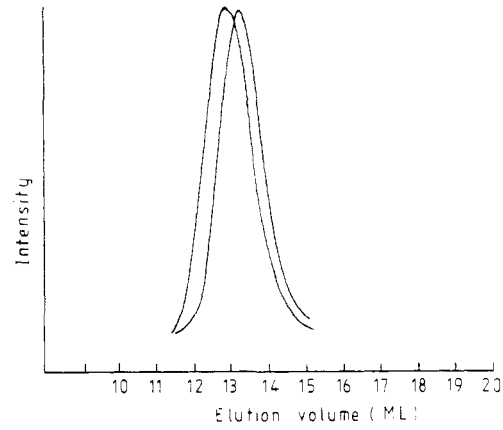


Figure 9. Typical GPC traces for a block copolymer: left curve, before aging; right, after aging.

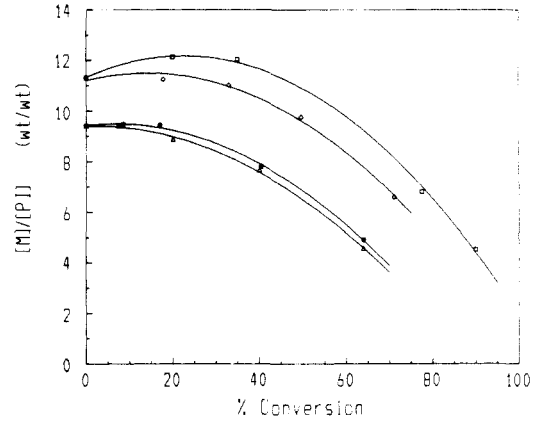


Figure 10. Evolution of the monomer–iniferter ratio during polymerization: *, MMA–PI_4; △, MMA–PI_2; □, styrene–PI_3; ◇, styrene–PI_2.

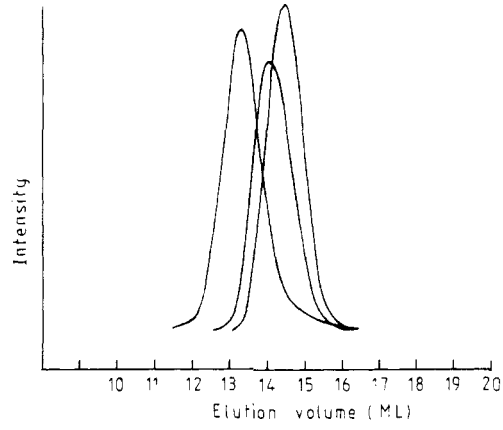


Figure 11. Representative GPC traces of block copolymers prepared at complete conversion: left curve, polystyrene–PDMS (PDMS = 8.2%); middle curve, PMMA–PDMS (PDMS = 9.5%); right curve, PMMA–PDMS (PDMS = 5.6%).

Table IV
Characteristics of the Block Copolymers Obtained at Different Conversion Levels Using PI_2

polymerizn conditions	conversn, %	PDMS content, wt %	mol wt before aging $\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_p \times 10^{-4}$	I	mol wt after aging $\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_p \times 10^{-4}$	I	av vinyl block length in unaged polym	no. of A–B blocks in the aged polym	[M]/[PI] residual
MMA, bulk	7.5	10.89	4.6	16.3	13.9	3.5	3.9	7.8	7.6	2.0	14 000	2.00	9.41
$[PI_2]$ = 10 w/v %	20	8.09	6.4	25.9	22.6	4.0	4.1	9.2	9.1	2.2	19 300	2.38	8.86
temp = 85 °C	40	6.58	8.0	21.0	17.7	2.6	4.7	9.5	9.3	2.0	24 135	2.45	7.65
[M]/[PI] = 9.4 by wt	64	4.27	10.3	32.3	24.5	3.1	5.2	11.1	10.7	2.1	38 100	2.81	4.55
styrene, bulk	17.8	8.60	10.7	27.0	19.2	2.5	7.0	18.7	3.9	2.6	18 000	5.60	11.25
$[PI_2]$ = 8 w/v %	33.0	8.36	11.7	31.5	22.2	2.7	7.8	19.8	15.8	2.5	18 540	6.30	11.01
temp = 90 °C	49.6	7.40	8.6	24.0	19.2	2.8	8.5	21.8	17.8	2.5	20 950	7.10	9.75
[M]/[PI] = 11.3 by wt	71.0	6.25	13.5	37.5	25.5	2.8	10.5	28.0	21.6	2.7	25 000	8.60	6.59

Table V
Characteristics of the Block Copolymers Obtained at Different Conversion Levels Using PI_3 and PI_4

polymerizn conditions	conversn, %	PDMS content, wt %	mol wt before aging $\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_p \times 10^{-4}$	I	mol wt after aging $\bar{M}_n \times 10^{-4}$	$\bar{M}_w \times 10^{-4}$	$\bar{M}_p \times 10^{-4}$	I	av vinyl block length in unaged polym	no. of A–B blocks in the aged polym	[M]/[PI] residual
MMA, bulk	8.5	11.40	6.0	13.5	8.6	2.2	4.4	9.1	8.3	2.0	36 500	0.95	9.46
$[PI_3]$ = 10 w/v %	17	10.80	8.7	18.7	16.4	2.1	6.9	12.0	10.6	1.7	38 700	1.21	9.43
temp = 85 °C	40	7.40	15.5	31.7	26.5	2.0	9.8	21.2	17.8	2.2	58 700	2.03	7.80
[M]/[PI] = 9.4 by wt	64	5.10	24.5	59.5	50.4	2.4	18.0	42.6	36.0	2.4	87 300	4.12	4.90
styrene, bulk	20	11.31	18.7	38.7	31.7	2.1	10.0	25.3	20.9	2.5	36 850	3.67	12.14
$[PI_4]$ = 8 w/v %	35	9.83	19.7	42.3	39.3	2.1	12.3	26.5	22.2	2.1	43 100	3.88	12.03
temp = 90 °C	77	7.14	22.9	61.7	56.1	2.7	21.2	45.8	39.3	2.1	61 100	6.87	6.81
[M]/[PI] = 11.3 by wt	90	7.60	19.4	51.6	45.3	2.6	19.1	50.1	44.2	2.6	57 150	7.73	4.52

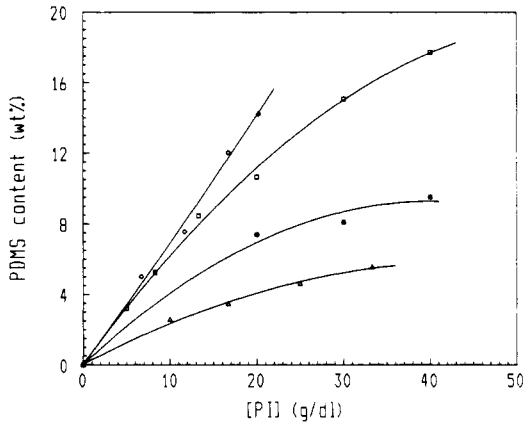


Figure 12. Copolymer composition as a function of PI concentration at complete monomer conversion: from bottom up, MMA–PI_2, MMA–PI_3, styrene–PI_3, and styrene–PI_2.

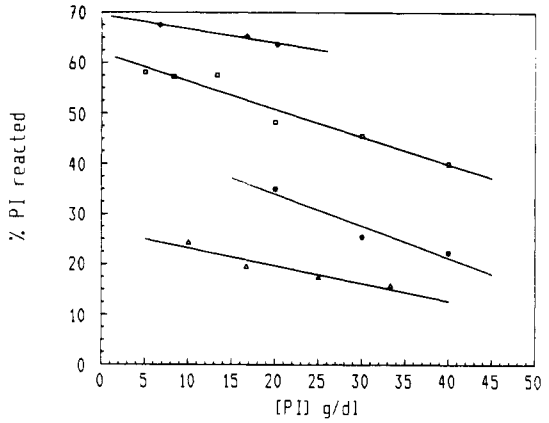


Figure 13. Variation of the extent of PI consumption with its concentration at complete monomer conversion: *, MMA–PI_3; △, MMA–PI_2; □, styrene–PI_3; ◇, styrene–PI_2.

block length per PDMS chain in the unaged polymer was also found to increase with conversion. It was possible to calculate the ratio of the unreacted PI and the residual monomer during the polymerization, and these data

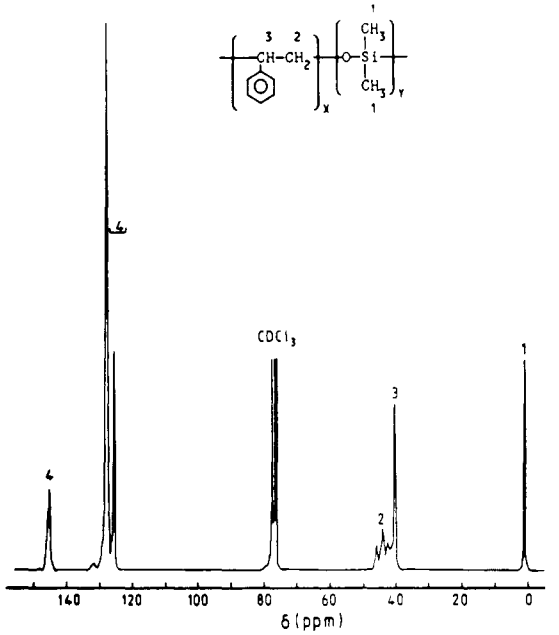


Figure 14. ^{13}C NMR ($CDCl_3$) of a polystyrene–PDMS copolymer.

are also carried on in Tables IV and V and graphically shown in Figure 10 for different cases. However, this calculation ignored the disulfide groups on the once-reacted PI. The [M]/[PI] ratio does not change for about 35% conversion for ST and 15% conversion for MMA, and thereafter it decreases. This may be due to the fact that the increasing viscosity of the medium causes restrictions on the reactivity of the PI and that, for subsequent polymerization, the iniferters already carried on the vinyl block are also utilized. The shape of the plots indicates a better functionalization for styrene. This is attributable to the better initiator efficiency in styrene coupled with its higher chain-transfer constant when compared to MMA as has already been observed in previous studies.[14] The decrease in [M]/[PI] ratio during polymerization should kinetically be expected to cause a

Table VI
Copolymerization Conditions and Copolymer Characteristics for MMA at Complete Conversion

polymerizn conditions	concn of PI, w/v %	PDMS in the copolym, wt %	mol wt $\bar{M}_n \times 10^{-4}$	mol wt $\bar{M}_w \times 10^{-4}$	mol wt $\bar{M}_p \times 10^{-4}$	mol wt I	av no. of A–B blocks	unreacted PI, %	av vinyl block length
PI_3, 85 °C	20	7.40	9.0	18.4	15.4	2.0	2.42	65	58 800
bulk	30	8.10	7.7	15.7	13.6	2.0	2.34	74.6	53 300
	40	9.50	6.7	12.7	11.5	1.8	2.32	77.7	44 750
PI_2, 85 °C	10	2.58	5.1	11.7	10.1	2.3	1.7	75.7	58 530
bulk	16.7	3.47	3.9	7.3	7.3	1.9	1.64	80.5	43 120
	25	4.61	3.1	5.9	4.9	1.9	1.46	82.6	32 060
	33.3	5.55	2.5	4.5	3.5	1.8	1.25	84.3	26 380

Table VII
Copolymerization Conditions and Copolymer Characteristics for Styrene at Complete Conversion

polymerizn conditions	concn of PI, w/v %	PDMS in the copolym, wt %	mol wt $\bar{M}_n \times 10^{-4}$	mol wt $\bar{M}_w \times 10^{-4}$	mol wt $\bar{M}_p \times 10^{-4}$	mol wt I	av no. of A–B blocks	unreacted PI, %	av vinyl block length
PI_3, 85 °C	5	3.21	19.3	38.0	26.3	2.0	1.86	41.9	137 200
bulk	8.3	5.25	14.4	27.2	22.1	1.9	2.53	42.8	82 180
	13.3	8.46	10.8	19.8	15.3	1.8	2.83	42.4	49 230
	20	10.65	8.4	15.6	12.3	1.8	2.86	51.8	38 170
	30	15.06	7.3	13.0	10.5	1.8	3.47	54.5	25 660
	40	17.70	7.2	11.6	9.6	1.6	3.75	60.0	21 140
PI_2, 85 °C	6.7	5.00	13.3	34.1	25.6	2.5	8.26	32.4	29 450
bulk	11.7	7.55	8.7	21.2	16.7	2.4	8.13	41.6	18 980
	16.7	12.00	7.6	18.5	14.5	2.4	11.20	34.8	11 340
	20.2	14.20	4.4	12.1	10.9	2.8	11.10	36.4	9 360

decrease in the vinyl block length as the polymerization advances, but it may in a sense be compensated by the reduced PI reactivity or reduced terminations in increasingly viscous medium. Block copolymers bearing as many as three A–B blocks were easily formed for MMA and up to eight A–B blocks for styrene. GPC analysis did not give any evidence for homopolymers formed by thermal polymerization, which would be expected to have very high molecular weights. Since the reaction system always contains residual PI even at very high conversion, their formation cannot normally be anticipated.

Block Copolymer Synthesis by Total Conversion. In order to have an understanding of the evolution of copolymer composition and structure at total conversion, polymerizations of MMA and ST were effected at 100% conversion using different concentrations of the PI. The polymerization was continued at high temperatures for 3 days to ensure complete monomer conversion and thermal destruction of all residual disulfide groups. The results are compiled in Tables VI and VII. A systematic increase in silicone content can be seen with a corresponding decrease in molecular weight and block numbers as the PI concentration increases. The average vinyl block length also decreases. Interestingly, all the copolymers produced at 100% monomer conversion had a satisfactory molecular weight distribution, a feature quite uncommon in high-conversion radical polymerization. In most of the cases, the polydispersity indices were in the range 2–2.5. Representative GPC curves at 100% conversion are shown in Figure 11. The variation of the copolymer composition with the iniferter concentration is represented in Figure 12. In all cases, good amounts of residual, unreacted but decomposed PI were recuperated. Only a fraction of the PI is consumed to form the copolymer. This fraction decreases as the PI concentration increases. The unreacted fraction is significant in the case of MMA. The enhanced consumption of PI by styrene is due to the reason already mentioned. This behavior is shown in Figure 13.

It becomes evident that large proportions of iniferters are required to synthesize silicon-rich block copolymers. The copolymers were characterized also by the ^{13}C NMR. A representative NMR can be found in Figure 14 for a poly(styrene-*b*-siloxane).

Table VIII
Details of Silicone–Acrylamide Copolymer Synthesis

reaction conditions	[PI], w/v %	conversn, %	silicone content, wt %	solubility in water
PI_1, THF	0.25	20	0.90	soluble
[M] = 2.11 mol·L^{-1}	0.5	18.6	1.11	soluble
temp = 70 °C	1.0	21	2.11	swelling
	1.5	15	5.76	insoluble
	2.0	19	7.10	insoluble
	2.5[a]	12	17.80	insoluble
PI_2, THF	1.5	14.5	2.90	soluble
[M] = 1.88 mol·L^{-1}	2.76	8.0	5.23	soluble
temp = 70 °C				after swelling

[a] At 80 °C.

Synthesis of Poly(acrylamide-*b*-siloxane). The synthesis of these polymers containing the two blocks differing widely in their solubility characteristics was realized by using PI_1 and PI_2 for the thermal polymerization of acrylamide. THF was used as the reaction medium. The polymer, when formed, precipitated out in the medium. Since in this case, the copolymer precipitates during the propagation, formation of multiblock polymer may not be effective. They may be to the most triblock copolymers, containing reactive thiuram disulfide groups. Table VIII gives the reaction conditions and the composition of the copolymers formed. They were characterized for their overall composition. Polymers with low silicone content were soluble in water, but the water solubility decreased drastically with a slight increase in silicone content. The water solubility depended also on the SCL. For SCL 625, polymers containing up to 5% were soluble whereas with SCL 4700 insolubility arose even at 2% PDMS. The water-insoluble polymers were found to be soluble in no other solvents. They had a tendency to swell slightly in THF. Under the synthetic conditions, the polymers have to be linear. Hence, the insolubility must be arising from the strong phase segregation between like segments, giving way to physical crosslinking. The soluble polymers must be able to serve as amphiphilic polymers for related applications.

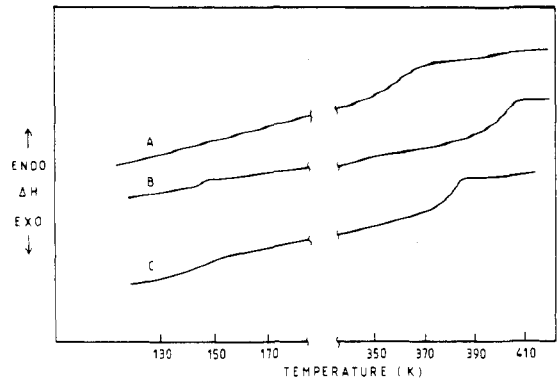


Figure 15. Glass transition behavior of different copolymer in DSC analyses: A, polystyrene–PDMS (PDMS = 14%, SCL 1550); B, PMMA–PDMS (PDMS = 9.5%, SCL 4600); C, polystyrene–PDMS (PDMS = 17.7%, SCL 4600). Heating rate 20 °C/min.

Physical Properties of the Block Copolymers. The copolymers retained the solubility characteristics of the vinyl polymers at low silicone content. But when the silicone content increased, they had a tendency to swell in heptane, a solvent for PDMS. DSC analyses showed the two distinctive T_gs of the elastic block, as well as the vitrous block pointing toward the microphase separation of the blocks for SCL 4500. But for shorter SCL (1550), the DSC analysis showed phase mixing, leading to a unique T_g. Figure 15 shows some typical DSC thermograms. In phase-separated polymers, both T_gs were slightly more elevated than those of the respective homopolymers. This increase is a further consequence of the microphase separation. Similar behavior has already been noted in silicone–vinyl block copolymers.[12,16]

Conclusion

Polymerization of vinyl monomers using PDMS-based thermal polymeric iniferters renders an alternate radical route to the synthesis of silicone–vinyl block copolymers. Choice of the desired PI concentration and proper reaction conditions can lead to the perfect formation of well-defined multiblock copolymers of narrow molecular weight distribution. This method is specially advantageous for low silicone content block copolymers. Since the dithiocarbamyl groups are thermally and chemically stable, at least to the same extent as the vinyl monomers and the block copolymer differs only in its mode of synthesis, they can be expected to have similar mechanical properties and thermomechanical profiles to the silicone–vinyl block copolymers already reported.[10,12]

Acknowledgment. Thanks are due to M. Scheer for the DSC analyses, Dr. P. Chaumont and M. Clauss for the GPC analyses, and M. Keyser and M. F. Peguet for the elemental analyses.

References and Notes

(1) Dean, J. W. *J. Polym. Sci., Polym. Lett. Ed.* **1970**, *8*, 677.
(2) Bajaj, P.; Varshney, S. K.; Misra, A. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 295.
(3) Juliano, P. C. U.S. Patent 3,663, 650, 1972; *Chem. Abstr.* **1972**, *77*, 127417m.
(4) Saam, J. C.; Ward, A. H.; Gordon Fearon, J. W. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1972**, *13*, 524.
(5) Varshney, S. K.; Beaty, C. L. *Org. Coat. Plast. Chem.* **1981**, *45*, 152.
(6) Chaumont, P.; Beinert, G.; Herz, J.; Rempp, P. *Eur. Polym. J.* **1979**, *15*, 459.
(7) Gagenbien, D.; Madec, P. J.; Marechal, E. *Eur. Polym. J.* **1985**, *21* (3), 271, 289, and 301.
(8) Auman, B. C.; Perec, V.; Schneider, H. D.; Jishan, W.; Canton, H. J. *Polymer* **1987**, *28* (1), 119.
(9) Yilgor, I.; Sha'aban, A. K.; Steckle, W. P., Jr.; Tyagi, D.; Wilkies, G. L.; McGrath, J. E. *Polymer* **1984**, *25* (12), 1800.
(10) Crivello, J. V.; Conlon, D. A.; Lee, J. L. *J. Polym. Sci., Polym. Chem. Ed.* **1986**, *24*, 1197 and 1251.
(11) Inoue, H.; Ueda, A.; Nagai, S. *J. Polym. Sci., Polym. Chem. Ed.* **1988**, *26*, 1077.
(12) Inoue, H.; Ueda, A.; Nagai, S. *J. Appl. Polym. Sci.* **1988**, *35*, 2039.
(13) Reghunadhan Nair, C. P.; Clouet, G.; Chaumont, P. *J. Polym. Sci., Polym. Chem. Ed.* **1989**, *27*, 1795.
(14) Reghunadhan Nair, C. P.; Clouet, G. *Makromol. Chem.*, in press.
(15) Reghunadhan Nair, C. P.; Clouet, G. *Polymer* **1988**, *29* (10), 1909.
(16) Williams, T. D. *J. Appl. Polym. Sci.* **1986**, *31*, 1293.
(17) Apfel, M. A.; Finkelmann, H.; Janini, G. M.; Laub, R. J.; Luhmann, B. H.; Price, A.; Roberts, W. L.; Shaw, T. J.; Smith, C. A. *Anal. Chem.* **1985**, *57*, 651.
(18) Brandrup, J.; Immergut, E. H. *Polymer Handbook*, 2nd ed.; 1975; Chapter IV, p 29. Korolev, A. Ya.; Andrianov, K. A.; Utesheva, L. S.; Vredenskaya, T. E. *Dokl. Akad. Nauk SSSR* **1953**, *89*, 65.
(19) Rogers, R. N.; Morris, E. D., Jr. *Anal. Chem.* **1966**, *38* (3), 412.
(20) Bloomfield, G. *J. Soc. Chem. Ind., London* **1949**, *68*, 66.
(21) Hallensleben, M. L. *Eur. Polym. J.* **1977**, *13*, 437.

Registry No. MMA, 80-62-6.