

Synthesis and Characterization of Five-Block Copolymers Prepared by Vinyl Pyrrolidinone and a Macro Initiator with Poly(dimethylsiloxane) and Polycaprolactone

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ABSTRACT: A new generation of a series of five-block copolymers of poly(dimethylsiloxane) (PDMS), polycaprolactone (PCL), and polyvinyl pyrrolidinone (PVP), (PVP-PCL-PDMS-PCL-PVP), are synthesized to obtain new polymeric systems containing PDMS with improved compatibilities. For this, a commercial reactive triblock copolymer of PCL and PDMS, namely (PCL-PMDS-PCL), was used as the starting material from which the peroxidic macroinitiator was prepared. By use of physicochemical methods, a five-block copolymer structure was confirmed, and its characterization was accomplished. Mechanical and thermal test results showed higher thermal resistances and increased toughness characteristics of the copolymer as compared with that of the component homopolymers. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **64**: 1961–1969, 1997

Key words: copolymers; five block copolymers, poly(dimethylsiloxane)

INTRODUCTION

Polysiloxanes, in particular, poly(dimethyl siloxane) (PDMS), drew considerable interest because of a number of inherent characteristics involved, such as the low glass transition temperatures, high chain flexibilities, and high thermal and ultraviolet (UV) stabilities, in addition to the well-known surface-modifying properties.¹ Their large molar volumes and low cohesive energy densities result at exceptionally low surface tensions, surface energies, and solubility parameters. Although PDMS is a good candidate for modification of other polymer surfaces and interfaces, it is highly immiscible with almost all other organic polymer systems²; and if PDMS is used by blending, it does not function properly. An effective way to increase compatibilities is certainly to form their copolymer systems; different block, segmented, and graft copolymers of siloxanes are al-

ready known;³ and a variety of macro initiators, macromonomers, and macromonomeric initiators have been reported for the synthesis of different block and graft copolymers.⁴

Polycaprolactones (PCL), on the other hand, are well known mainly because of their miscibilities for a wide range of organic polymers. Yilgör et al.² and Lovinger et al.,³ in this context, have synthesized a series of triblock (caprolactone–siloxane) copolymer systems to get compatible polymeric materials bearing interesting properties of PDMS and polycaprolactone.

In this study, a new generation of a series of five-block copolymers of PDMS are synthesized to obtain new polymeric systems of the latter with improved compatibilities. For this, a commercial reactive triblock copolymer of (PCL-PDMS-PCL) was used as the starting material in the polymerization of water-soluble vinyl pyrrolidinone (VP) by a stepwise procedure.^{5–7} The hydroxyl-terminated triblock copolymer used was end-capped with an aliphatic diisocyanate in the first step, which was then reacted with an aliphatic hydro-

Table I Preparation Conditions and Characteristics of Macroinitiator

Sample	$\frac{[-\text{NCO}]}{\text{PDMS}}$	Isocyanate wt % of Capped Tegomer	M_n (g/mol)	$\frac{[-\text{OOH}]}{[-\text{NCO}]}$	Peroxide (wt %)
Prepolymer (Tegomer H-Si 6440)					
PCL-PDMS-PCL 2, 3, 2 ^a	—	—	6500 ± 600	—	—
Urethane	3.00	1.21 ca. 1.15	6940 ca 7300	—	—
MI	—	—	7100 7440	3.10	0.90 ca. 0.86

^a Numbers designate molecular weight averages of PCL, PDMS, and PCL blocks in thousands, determined by end-group analysis by the supplier.

Table II Preparation Conditions and Some Characteristics of the (PVP-PCL-PDMS-PCL-PVP) Five-block Copolymer (Copolymer 1)

Initial Composition (wt %)		Yield (%)	$[\eta]$ (dL/g)	$M_v \times 10^{-6}$ (g/mol)	$M_w \times 10^{-4}$ (by ICP) (g/mol)
MI	VP				
2.2	97.8	32	1.47	1.15	2.42

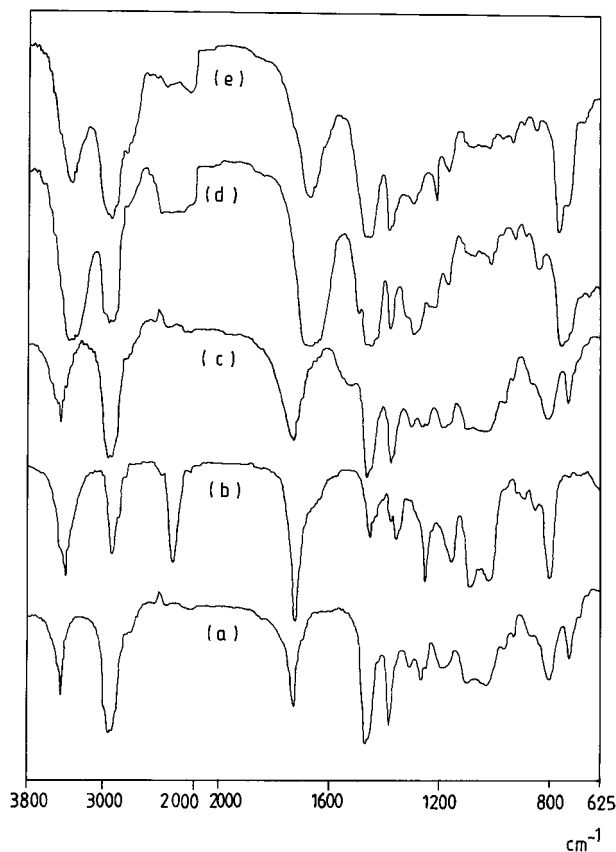


Figure 1 IR spectra of (a) Tegomer H-Si 6440, (b) urethane, (c) MI, (d) homo PVP, and (e) PVP-PCL-PDMS-PCL-PVP (the five-block copolymer, Copolymer 1). In all, nujol is used as the milling agent.

peroxide to prepare the peroxidic macroinitiator. The five-block copolymer (PVP-PCL-PDMS-PCL-PVP) obtained was characterized by physicochemical, mechanical, and thermal methods.

EXPERIMENTAL

Materials

The α,ω dihydroxy polycaprolactone-poly(dimethylsiloxane) (PCL-PDMS-PCL) triblock copolymer used was a commercial product of Goldschmidt Chemical Corp. (Tegomer H-Si 6440 with $M_n = 6500 \pm 600$; M_w (PDMS) = 3000; and PCL endblocks = 2000 g/mol). It was dried at 70°C in a vacuum oven for 48 h before use.

Isophorone diisocyanate (IPDI), a product of Fluka AG, was used without further purification. The purity determined by isocyanate analysis was 95.1%.

The t-Butylhydroperoxide (t-BHP) used was also a product of Fluka AG. It was distilled under reduced pressure. The peroxide content was 93.3%. It was used after drying over anhydrous magnesium sulphate.

Dibutyltin dilaurate (T-12) was a product of Fluka AG. It was used as a catalyst without purification.

N-vinyl pyrrolidinone (a product of Fluka AG) was washed with 10% aqueous NaOH solution,

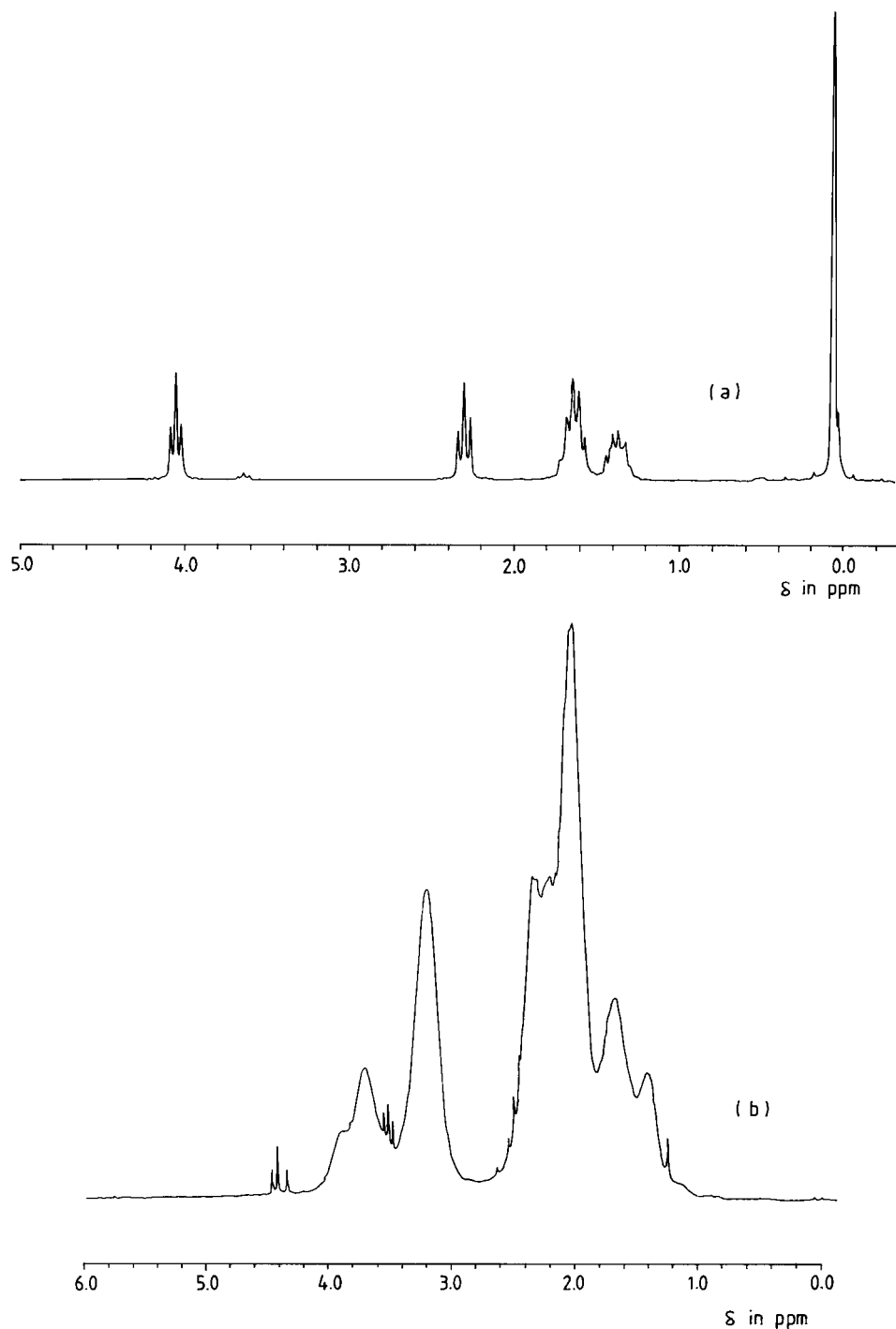


Figure 2 ¹H NMR spectrum of (a) Tegomer H-Si 6440, (b) homo PVP, and (c) Copolymer 1.

dried over CaCl₂, and distilled at 1–2 mm Hg at 55°C.

All solvents used during synthesis reactions were products of Merck AG. They were carefully dried over molecular sieves (Linde type 5A), followed by fractional distillation.

Analysis and Tests

Isocyanate analysis was performed by reacting a weighed amount of the material with standard dibutyl-amine solution in toluene and by back-titrating the excess amine with standard HCl.⁸

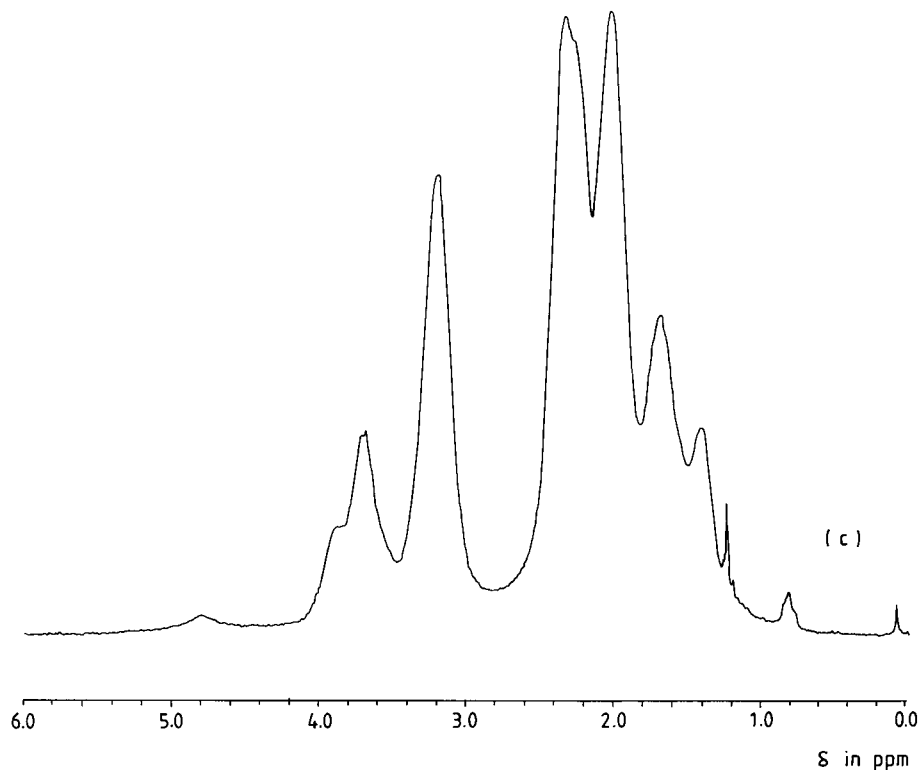


Figure 2 (Continued from the previous page)

Peroxide content was determined by standard iodometric method.⁹

Infrared (IR) spectra were collected by a Pye Unicam SPI025 Model Grating IR Spectrometer and during nuclear magnetic resonance (NMR) studies; a Bruker AC 200C, 200 MHz spectrometer was employed. An inductively coupled plasma (ICP) spectroscope (Atomscan 25, U.S.A. Thermo Jarrell Ash Argon) was used during Si content determination of the copolymer.

Stress-strain tests were done by use of Tensilon (Toyo Measuring Instruments Co., Ltd.) UTM II Tester at room temperature with a constant cross-head speed of 1 mm/min.

Thermal analysis were done by TA Instruments 910S (DSC) and 951 (TGA) series equip-

ment, with constant heating rates of $10^{\circ}\text{C min}^{-1}$ and with various selected heating rates for the samples, respectively.

Procedure

Preparation of Macroinitiator

The dihydroxyl-terminated prepolymer (PCL-PDMS-PCL) and the IPDI were reacted at 70°C for 96 h in a 1,2-dichloroethane solution under a blanket of dry nitrogen atmosphere. The molar ratio of diisocyanate to prepolymer was held as three in order to prevent undesired chain extensions. The resulting product was precipitated with dry petroleum ether ($40\text{--}60^{\circ}\text{C}$ fraction) in order to separate

Table III Mechanical Properties of Copolymer 1 and Homo PVP

Sample	UTE (%)	Tensile Strength (MN/m^2)	UTS (MN/m^2)	Young's Modulus (GN/m^2)
Homo PVP	10.5	33.2	20.4	0.75
Block Copolymer 1	13.2	22.6	19.6	0.39

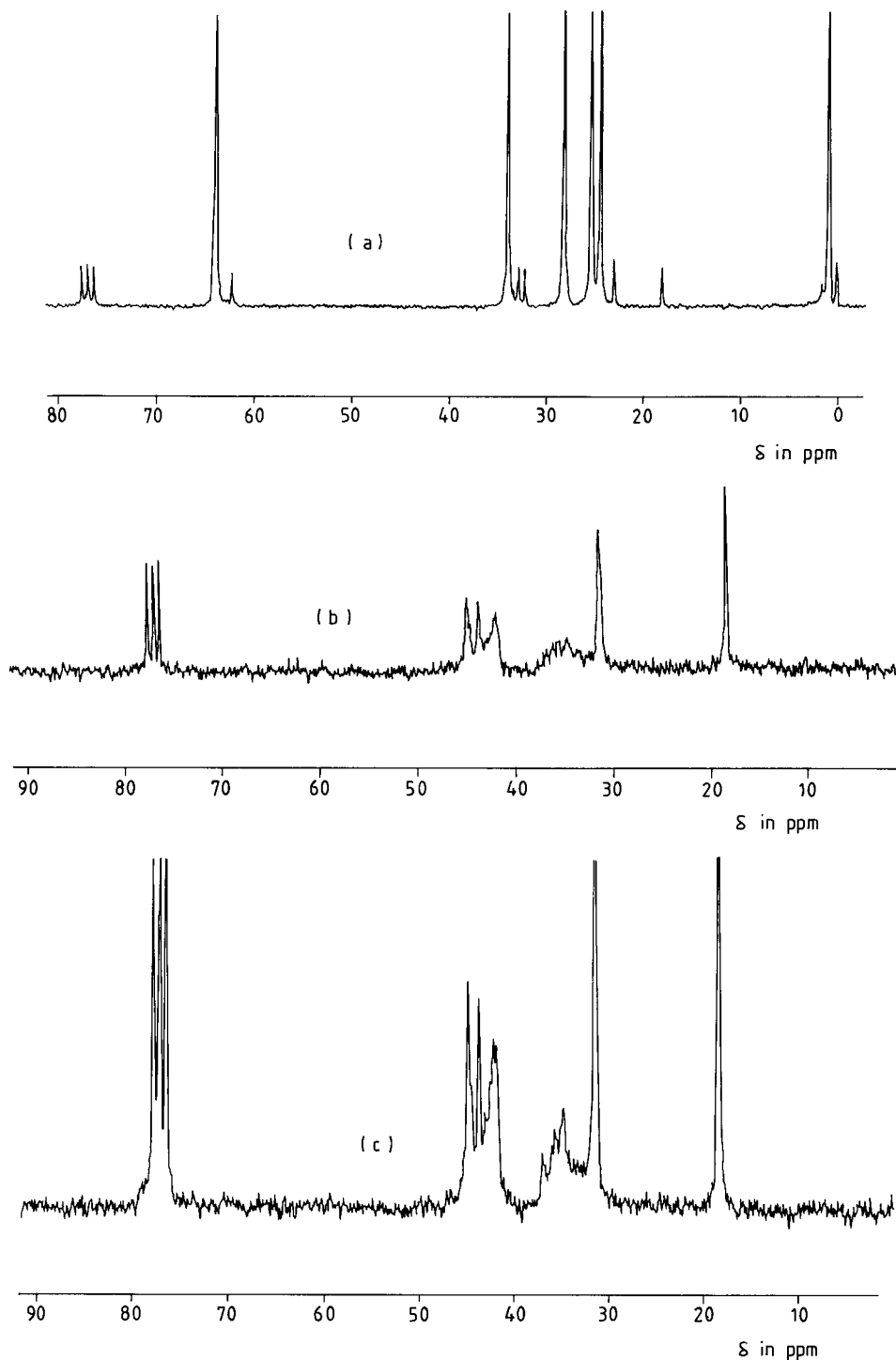


Figure 3 ^{13}C NMR (partial) spectrum of (a) Tegomer H-Si 6440, (b) homo PVP, and (c) Copolymer 1.

the excess of diisocyanate and was dried *in vacuo* at room temperature overnight. The isocyanate content of the end-capped product was determined by end group titration of isocyanates. The calculated

molecular weights were consistent with the ones expected from the theoretical formula.

In the second step, the diisocyanate-terminated siloxane was reacted with *t*-butylhydroperoxide in

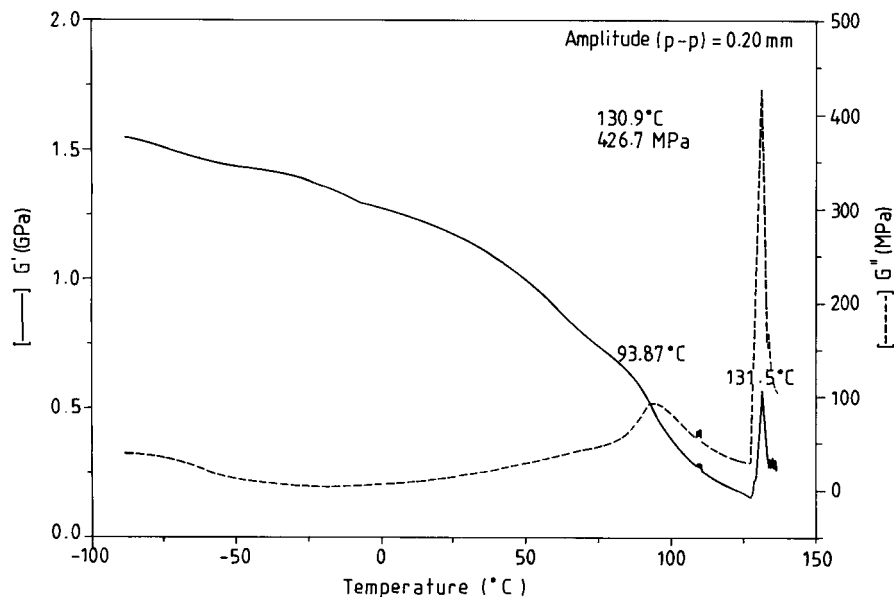
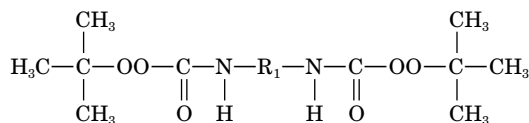


Figure 4 DMA response of Copolymer 1.

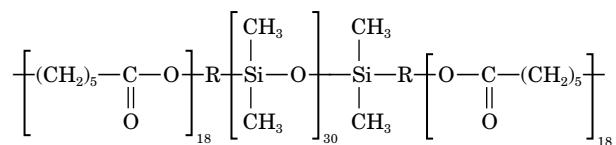
methylene chloride. A few drops of T-12 catalyst was then added to the reaction mixture. This procedure was also carried out under a nitrogen blanket at room temperature, in darkness, for 100 h. In the system, the molar ratio of t-butylhydroperoxide to isocyanate ($-\text{OOH}/-\text{NCO}$) was always kept at a value that is higher than three in order to prevent chain extension.

The resulting product was precipitated with acetonitrile, dried in vacuum at room temperature. The peroxide content, which was determined by iodometric titration, was identical with the theoretically expected value.

The structural formula of the macroinitiator expected is as follows:



where (R_1) is:



Synthesis and Characterization of the Copolymer

During the polymerization of VP, the radicalic macroinitiator (MI) was used. The copolymers were synthesized in bulk (or in ethanol solu-

tions). For this, weighed amounts of MI were dissolved in predetermined amounts of VP. Ethanol, the polymerization solvent, was then added to the mixture. The mixture was degassed, and the solution was distributed into PyrexTM tubes through the vacuum line. All tubes were immersed in thermostatically controlled oil baths at 60°C, and polymerization was carried out for 100 h. After this, the solid product was dissolved in ethanol, precipitated in benzene, and filtered and dried *in vacuo* at 30°C for 48 h.

Specific viscosity of copolymers were measured at 25°C in chloroform. The following viscosity-molecular weight relationship was used:¹⁰

$$[\eta] = 1.94 \times 10^{-4} \times M_v^{0.64} \text{ (dL/g)}$$

The viscosity-average molecular weight calculated by use of this relationship is expected to be an approximate value because the preceding relation was forwarded for pure PVP.

The intermediates and the products were characterized also by IR, ¹H, and ¹³C NMR spectroscopic methods, as well as by thermal and mechanical tests, as outlined above in the Analysis and Tests section. Polymeric films used in most of these tests were prepared from solution by use of a 50 : 50 (vol %) mixture of dichloromethane and methanol.

RESULTS AND DISCUSSION

In this study, a new-generation peroxy-carbamate MI was prepared and characterized by reacting

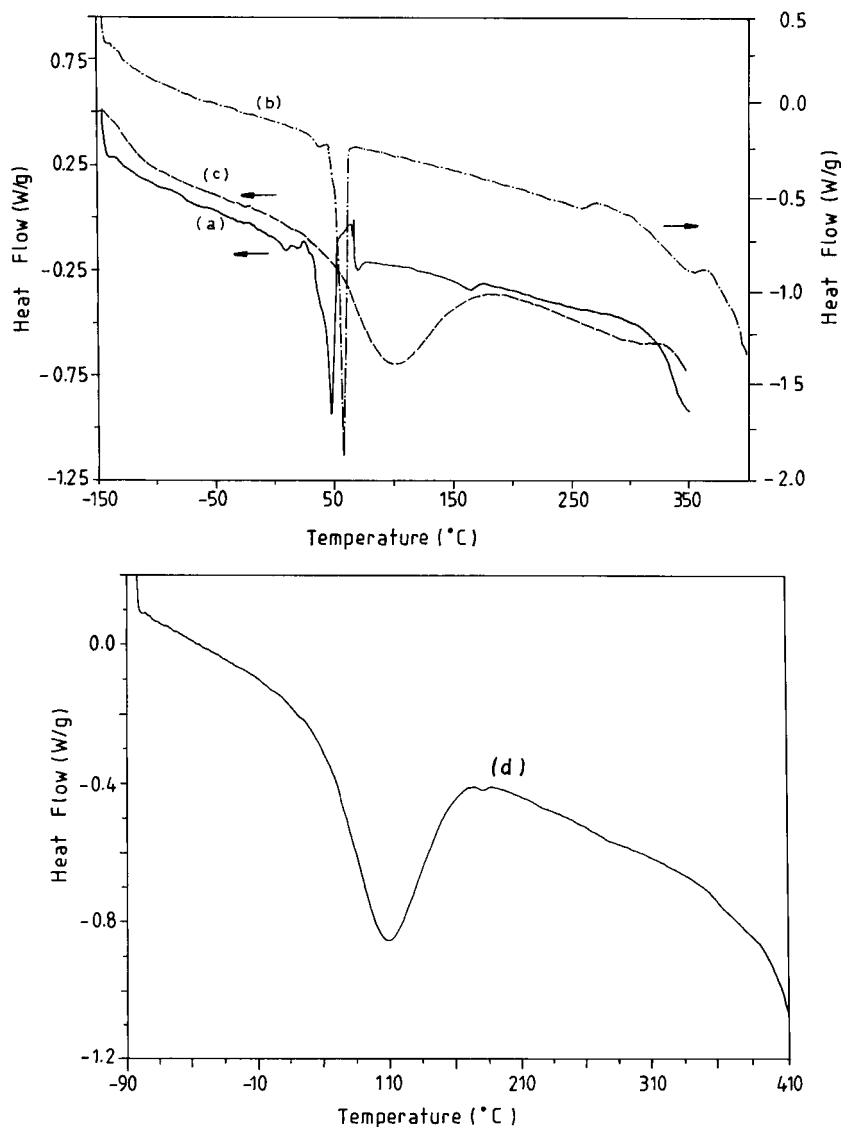


Figure 5 DSC thermograms of (a) homo PCL, (b) Tegomer H-Si 6440, (c) homo PVP, and (d) Copolymer 1.

isocyanate-capped PMDS and t-BHP, and the MI was used as the starting material for the synthesis of five-block copolymers (PVP-PCL-PMDS-PCL-PVP). Experimental data on the preparation of the MI and copolymer are given in Tables I and II, respectively. In the latter and in other test results sections, data for one copolymer product (labelled Copolymer 1) will be presented since complete characterization is available only for this one at the moment.

In this series of studies, a PVP homopolymer (with $[\eta] = 0.537$ dL/g at 25°C in chloroform) was also prepared by use of AIBN initiator ($[I]_0 = 3.44 \times 10^{-3}$ mol/L in bulk), for comparison purposes.

Intermediates and products obtained were

characterized by IR spectroscopy. In the IR spectra of tegomer H-Si-6440 [Fig. 1(a)], the peaks from OH (at 3500 cm^{-1}), Si-O (at 1024 cm^{-1}), and Si-CH₃ (at 1260 and 800 cm^{-1}) are clearly seen, the latter two of which are characteristic peaks for PMDS. The peak at 1730 cm^{-1} is from C=O group of PCL. The OH absorption peaks were disappeared at the end of the capping reaction with diisocyanate, as expected [Fig. 1(b)]. There is a peak at 2280 cm^{-1} (stretching vibration of —NCO), which is the principal absorption peak for isocyanate groups (urethane). In the second reaction step, disappearance of this peak certainly indicates the formation of the MI, which is also illustrated in Figure 1(c). The IR of homo-

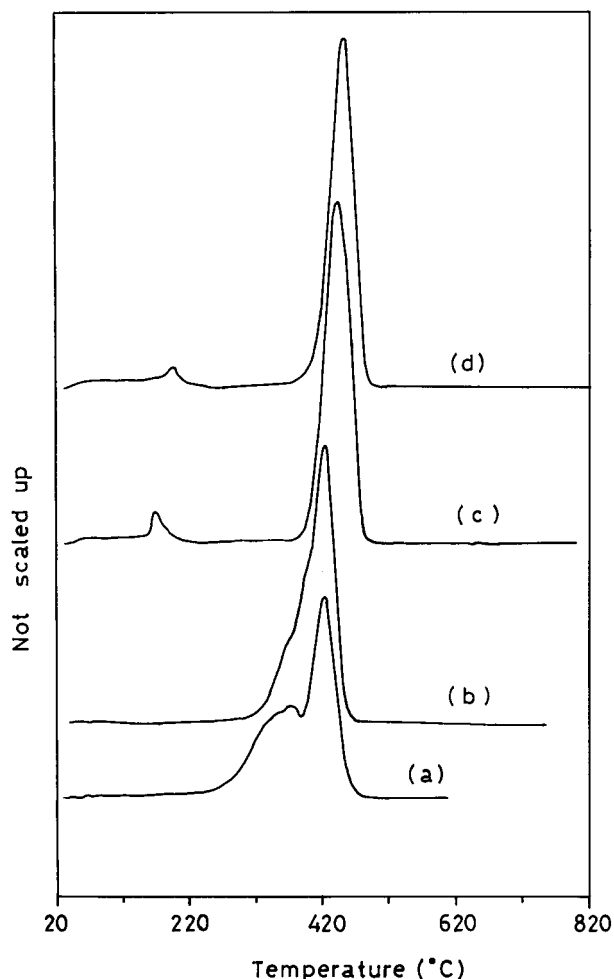


Figure 6 TGA Thermograms of (a) homo PCL, (b) Tegomer H-Si 6440, (c) homo PVP, and (d) Copolymer 1. The heating rate is 10°C/min.

PVP is also shown in the figures [Fig. 1(d)]; for comparison purposes with that of the copolymer [Fig. 1(c)]. The main absorption peaks shown in the spectra proves the incorporation of MI into the structure; hence, it also provides a definite evidence for the formation of block copolymers.

In the IR spectra of Copolymer 1 [presented in Fig. 1(e)], urethane peaks around 3440 cm^{-1} were observed for all copolymer samples, which is known as due to —NH stretching in the —NH—CO— group in the MI.

The ICP studies of the block copolymer have resulted in 17.4 ppm Si in the sample ($C = 0.4791\text{ g}/100\text{ mL}$), which yields 0.36% Si in the sample. Since 31 moles of Si is known to exist in the sample, from this, the molecular weight of the copolymer can be estimated as 242,000 g/mol.

This finding can also be supported by ^{13}C NMR studies, which yields the block copolymer structure in the ratio of 1 : 35 of middle block MI (PCL-PMDS-PCL) to VP segments. In the ^{13}C NMR studies, the NOE (Nuclear Overhauser Effect)-suppressed ^{13}C spectra of copolymer show the ratio very clearly and quantitatively. The ^{13}C chemical shifts are certainly an early assignment to the structure supposed in relation to the proton NMR spectra^{11,12} (Figs. 2 and 3).

Results of static mechanical test for the block copolymer and homo-PVP films are obtained from the stress-strain curves, and they are presented in Table III. As it is seen from the table, the five-block copolymer increased toughness of PVP appreciably [where an increase in the percentage of ultimate tensile elongation (UTE) is by a 25% change in ultimate tensile strength (UTS)] by retaining high a UTS value of PVP, although the modulus is decreased twice. Dynamic mechanical analysis results for the copolymer (Fig. 4) points out two transitions, one around 96°C and the other at 130°C; the latter of which obviously is

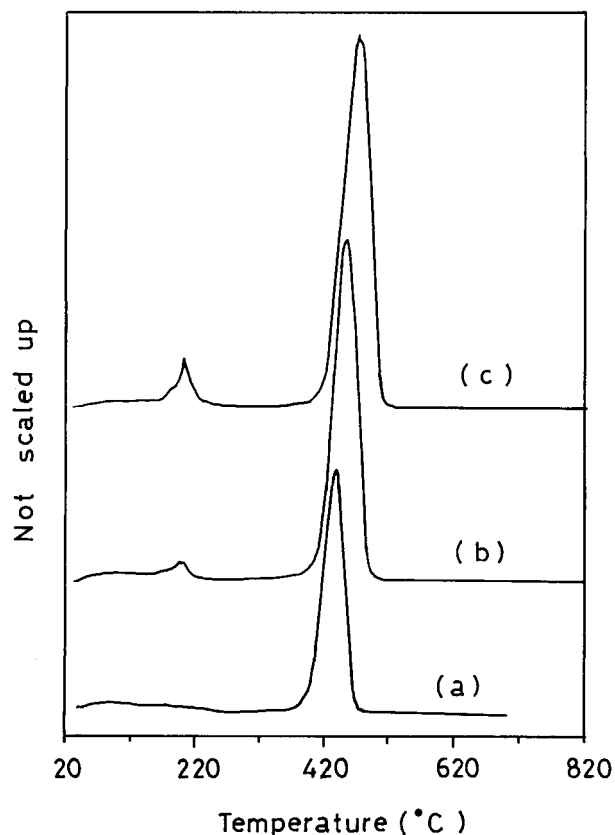


Figure 7 TGA thermograms of Copolymer 1 with various heating rates: (a) 5, (b) 10, and (c) 25°C/min.

Table IV Activation Energy of Thermal Decompositions for Component Homo and Block Copolymers and Copolymer 1 Calculated From Primary Peaks

Sample	Activation Energies (E_a) (kJ)	
	Kissinger	Flynn–Wall
PCL	170.5	173.1
Tegomer H-Si 6440	121.7	126.7
Homo PVP	149.3	153.3
Block Copolymer 1	193.5	195.4

the highest temperature usable for differential scanning calorimetry (DSC) for the copolymer, although it is not too significant; nevertheless, it should correspond to the onset of melting point/thermal decomposition.

Thermal analysis studies have yielded transition temperatures [as determined from DSC thermograms (Fig. 5(a)–(c))] and thermal decomposition data (from TGA studies; see Figs. 6 and 7) for PCL, tegomer H-Si 6440, PVP homo, and Copolymer 1. TGA results clearly indicate thermal stability gain for the five-block copolymer system synthesized as compared with that of component polymers and copolymers, with about a 5% secondary loss around 170°C and the primary loss at around 440°C. If TGA data of homo- and triblock copolymers are considered, maximum thermal decomposition temperatures obtained are all well below 440°C, while the secondary loss peak observed is most probably due to PVP end groups in the five-block copolymer. If energy of activation for thermal decomposition (E_a) values, obtained by use of Kissinger¹³ and Flynn–Wall^{14,15} methods separately (Table IV), are considered, one also concludes the apparent contribution of PCL to the thermal stability of the five-block copolymer. More comprehensive thermal studies with other series of five-block copolymers are underway, the results of which will be the subject of another communication.

CONCLUSIONS

From the results presented above, the following conclusions can be drawn. 1) The five-block copolymer (PVP-PCL-PDMS-PCL-PVP) can be synthesized by use of (PCL-PDMS-PCL) as the starting material, from which the peroxidic MI can be prepared; and 2) the five-block copolymer synthesized is much tougher mechanically and has a better thermal resistance value than the component homo/copolymers.

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