

Poly(vinyl Chloride)–Polyol (AB)_x Block Copolymers: Synthesis, Characterization, and Mechanical Properties

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Synopsis

Poly(vinyl chloride)–polyol (AB)_x block copolymers have been prepared by the condensation polymerization of low-molecular-weight hydroxy-terminated poly(vinyl chlorides) (PVC) and diisocyanate-capped polyester and polyether diols. The difunctional poly(vinyl chlorides) were synthesized by ozonization of commercial resin followed by metal hydride reduction. The (AB)_x block copolymers, which contained 3000 or 4300 molecular weight PVC block sizes and 1000–2000 molecular weight polyol segments, had a wide range of mechanical properties, depending on overall polymer structure. Tensile strengths ranged from 7.8 to 31.5 MPa, elongations from 125% to 610% and torsional stiffness temperatures (T_f) from 25°C to –22°C.

INTRODUCTION

The flexibilization of poly(vinyl chloride) has traditionally been achieved by compounding the resin with various low molecular weight materials, i.e., plasticizers. The externally plasticized resins do not retain the desired mechanical properties on long-term aging since the plasticizer migrates out and inflexibility returns. Chemical approaches to permanency of plasticization, that is, internal plasticization, have included copolymerization with a variety of monomers with marginal results. A conceivably better approach would be to synthesize a poly(vinyl chloride) block copolymer with soft segments to aid in making the polymer less rigid. Block copolymers of this type can be made by first preparing a prepolymer that can generate a free radical source and then combining it with vinyl chloride under polymerization conditions. For example, macroazobitriles have been prepared^{1,2} by the reaction of 4,4'-azo-bis-4-cyano-valerylchloride and hydroxy-terminated polyethers. Thermal decomposition of the azo linkages under either emulsion or solution conditions in the presence of vinyl chloride yielded a mixture of AB and ABA block copolymers. These polymers had lower torsional stiffnesses than unplasticized poly(vinyl chloride) but still required external plasticization to equal the flexibility of plasticized poly(vinyl chloride).³ The major difficulty was with the polymerization process itself. A maximum of 15 wt % poly(ethylene oxide) could be incorporated into the block copolymer. When large polyethers were used as part of the macroazobitrile, excessive grafting of vinyl chloride on the polymer backbone took place. Other workers have had similar difficulties in synthesizing poly(vinyl chloride) block copolymers by free radical polymerization.^{4,5}

To increase the soft segment content of the block copolymers, a synthetic method for making (AB)_x block copolymers was necessary. This approach re-

quired the use of low molecular weight poly(vinyl chloride) with reactive end groups. Michel⁶ had reported the synthesis of low molecular weight difunctional carboxy-terminated poly(vinyl chloride) by the ozonization of medium molecular weight polymer. This procedure was particularly attractive in that functionalities very close to two and narrow weight ranges could easily be obtained. Attempts by us to convert the acid end groups to acid chlorides and subsequently to polymerize by reaction with hydroxy-terminated polyols yielded only low to medium molecular weight block copolymers. Similar results have been recently reported by Michel and co-workers⁷ when they condensed acid chloride terminated poly(vinyl chlorides) with hexamethylenediamine and 1,6-hexanediol. This is probably due to the difficulty of converting the acid end groups to acid chlorides, a reaction that does not go to completion in these polymeric systems, as evidenced by the infrared maximum at 1735 cm^{-1} due to unreacted acid groups. It has been found that reduction of the acid end groups to hydroxy groups followed by reaction with isocyanate-capped polyols yields high molecular weight $(AB)_x$ block copolymers. In this paper are reported the synthesis, characterization, and properties of a series of block copolymers where A is poly(vinyl chloride) and B is poly(tetramethylene oxide), poly(propylene oxide), poly(tetramethylene adipate), or polycaprolactone.

EXPERIMENTAL

Materials

Poly(propylene oxide) (THANOL® PPG-2000), poly(tetramethylene oxide) (TERACOL®-1000 and -2000), poly(tetramethylene adipate)(Formrez L8-71), and polycaprolactone (NIAX® PCP-0240) diols were dried prior to use for 24 h at 100°C and 0.1 torr. The methylene-bis-(4-phenylisocyanate) was purified by heating to 100°C and removing the unmelted portion by filtration. Toluene diisocyanate and methylene bis(4-cyclohexyl-isocyanate) were distilled prior to use. *N,N*-Dimethylformamide was distilled from calcium hydride and stored over 3-Å molecular sieves. Other chemicals and solvents were used as received. Ozone was generated from oxygen by means of a model T-408 Welsbach Laboratory Ozonator. Two commercial grade poly(vinyl chloride) (PVC) resins, Monsanto Opalon and Diamond Shamrock P-40, were used.

Ozonization of Poly(vinyl Chloride)

Suspension grade poly(vinyl chloride) was suspended in various chlorinated solvents contained in a glass reaction flask and ozonized for specific times at different temperatures with a constant ozone concentration. The results of these ozonizations are summarized in Table I.

Synthesis of Acid-Terminated Poly(vinyl Chloride)

Various low molecular weight acid terminated poly(vinyl chlorides) were synthesized by a procedure similar to that reported by Michel,⁶ in which commercial grade poly(vinyl chloride) was ozonized at elevated temperatures in a chlorinated solvent. In a typical preparation suspension grade PVC (4500 g)

TABLE I
 Ozonization of PVC in Various Solvents

	Polymer				
	1	2	3	4	5
PVC	100	100	100	100	100
Solvent ^a	Cl ₄ E	Cl ₂ E	Cl ₃ E	CHCl ₃	DCB
Wt % PVC	5	5	5	5	5
Temperature (°C)	70	70	80	60	100
Ozone concn (mg/min)	62	62	62	62	62
Ozonization (h)	20	20	24	20	28
Inherent viscosity, ^b final	0.10	0.14	0.40	0.23	0.17
\bar{M}_n^c	2300	3000	15,600	7300	3700
Acid number	44	35	6	15	42
Functionality	1.8	1.9	1.6	1.9	2.7
Oxygen, % calculated	2.55	2.00	0.33	2.37	2.03
Oxygen, % found ^d	3.90	2.64	0.79	4.32	2.88

^a Cl₄E, 1,1,2,2-tetrachloroethane; Cl₂E, 1,2-dichloroethane; Cl₃E, 1,1,1-trichloroethane; DCB, 1,2-dichlorobenzene.

^b THF at 30°C.

^c Determined from vapor phase osmometry and gel permeation chromatography.

^d Determined from elemental analysis.

was suspended in 1,2-dichloroethane (40 L) contained in a 50-L glass reaction flask. The stirred mixture was heated at 70°C and ozone was introduced at a rate of 200 mg/min with an oxygen flow rate of 4 L/min. Ozone concentrations were determined by iodometric titrations.⁸ The exhaust gases were passed through sodium hydroxide scrubbers before venting up the exhaust hood. As the molecular weight decreased, the PVC gradually became soluble in the 1,2-dichloroethane (DCE). Samples were withdrawn at intervals and the inherent viscosity determined in tetrahydrofuran at 30°C. A viscosity of 0.10 corresponded roughly to a molecular weight of 3000. After ozone introduction had been terminated, oxygen was bubbled through the solution for several hours to remove all traces of ozone and to complete the oxidation reaction. The resulting acid-terminated poly(vinyl chloride) was isolated by concentrating the solution to one-half the original volume and slowly pouring the solution into rapidly stirred methanol. The precipitated polymer was recovered by filtration and washed several times with water and with methanol, before drying to a constant weight. The yield of carboxy terminated polymer was 3735 g. The results of four ozonizations are shown in Table II.

Synthesis of Hydroxy-Terminated Poly(vinyl Chloride)

The terminal acid groups could be reduced to hydroxy groups by a number of metal hydrides or diborane. In a typical reduction a solution of acid-terminated PVC (1000 g, $\bar{M}_n = 4300$) in tetrahydrofuran (22 L) was added via a metering pump to a suspension of lithium aluminum hydride (70 g) in tetrahydrofuran (15 L). The solution was added at a rate of 250 mL/min and an exotherm to 35°C was noted. After all the carboxy terminated PVC had been added, the solution became very viscous and gelled. After standing at room temperature overnight, the excess lithium aluminum hydride was destroyed and the gel dis-

TABLE II
Preparation of Acid Terminated PVC by Ozonization^a

	Polymer			
	A-15	A-20	A-40	A-45
PVC, g	1500	2000	4000	4500
Wt % PVC	5	10	10	9
Ozone (mg/min \pm 5 mg)	110	150	185	200
Time of ozonization (h)	60	110	135	150
Inherent viscosity, final	0.10	0.10	0.18	0.16
\bar{M}_n	3000	4300	6400	4400
Acid number	36	24	15	23
Functionality	1.8	1.7	1.8	1.9
Oxygen, % calculated	2.02	1.35	0.85	1.28
Oxygen, % found	2.98	1.92	1.23	2.03

^a Reactions run at 70°C in 1,2-dichloroethane.

solved by the addition of concentrated hydrochloric acid. The addition of an excess of acid (approximately 310 mL) resulted in a quick separation of the inorganic salts to the bottom of the flask, thus allowing for easy decantation of the clear liquid. The solution was concentrated to one-fourth its original volume and was poured into vigorously agitated water. The precipitated polymer was recovered by filtration, washed to neutral pH with water, washed with methanol, and dried to a constant weight of 914 g. The results of four reductions are summarized in Table III.

Synthesis of Poly(vinyl Chloride)-Polyol (AB)_x Block Copolymers

The block copolymers were made by condensing hydroxy terminated PVC with diisocyanate-capped polyols. For a typical preparation, poly(tetramethylene oxide) (600 g, 0.3 mol) was placed in a carefully dried 22-L flask equipped with a high-speed stirrer, nitrogen inlet tube, thermometer, and addition funnel. The polyol was warmed to 80°C and methylene-bis-(4-phenylisocyanate) (153 g, 0.61 mol) was added in one portion. The temperature rose to 100°C and stirring was continued for 4 h before the isocyanate (NCO) content was determined (Table IV). Dry *N,N*-dimethylformamide (1500 mL), dibutyltin dilaurate

TABLE III
Hydroxy-Terminated PVC^a

	Polymer ^b			
	H-15	H-20	H-40	H-45
Inherent viscosity	0.13	0.17	0.20	0.16
\bar{M}_n (VPO)	3000	4300	6400	4400
\bar{M}_n (GPC)	4300	6400	8500	6000
\bar{M}_w (GPC)	8200	13,000	15,000	10,000
\bar{M}_w/\bar{M}_n	1.9	2.1	1.8	1.7
Oxygen, % calculated	1.01	0.70	0.48	0.64
Oxygen, % found	1.24	1.44	0.85	1.12
Chlorine, % calculated	56.09	55.98	56.31	56.16
Chlorine, % found	54.23	55.61	56.19	54.38

^a Reductions carried out in tetrahydrofuran using lithium aluminum hydride.

^b Same sequences as Table II.

TABLE IV
 Poly(vinyl Chloride)-Polyol (AB)_x Block Copolymers

Polymer	PVC ^a block \bar{M}_n	Polyol	Polyol ^b M_n	Diisocyanate	Isocyanate-capped polyol		Inherent ^c viscosity	Block copolymer		Weight % polyol Calcd. Found ^e	
					% NCO calculated	% NCO found		\bar{M}_n^d	\bar{M}_w^d		
PVC-PPO-1	3000	PPO	2000	MDCI	3.36	3.79	0.61	19,800	41,300	36	33
PVC-PPO-2	3000	PPO	2000	MDI	3.33	3.29	0.67	30,600	80,100	36	39
PVC-PTMA-1	4300	PTMA	1900	TDI	6.47	5.19	0.96	37,400	89,300	29	32
PVC-PTMA-2	3000	PTMA	1900	MDI	3.50	3.61	0.89	27,700	90,400	34	41
PVC-PTMO-1	3000	PTMO	1900	MDI	3.48	3.21	0.81	21,100	60,400	34	43
PVC-PTMO-2	3000	PTMO	1900	MDCI	3.79	3.88	0.83	23,100	70,200	34	43
PVC-PTMO-3	4300	PTMO	1000	TDI	3.54	3.60	0.75	23,200	61,500	18	24
PVC-PCL-1	4300	PCL	2000	MDI	3.36	3.68	0.72	30,100	90,100	30	32
PVC-PCL-2	3000	PCL	2000	MDI	2.42	2.30	0.76	31,600	126,000	47	44

^a Vapor phase osmometry.^b Hydroxyl number determination.^c 0.5 g/dL in tetrahydrofuran at 30°C.^d Gel permeation chromatography.^e Based on elemental analysis.

(0.5 g), and triethylenediamine (1.0 g) were added to the isocyanate-capped polyol solution. To this vigorously stirred solution at 80°C a solution of hydroxy-terminated poly(vinyl chloride) (900 g, 0.30 mol) dissolved in dry DMF (4500 mL) was added at the rate of 75 mL/min. When the solution showed a rapid increase in viscosity, as indicated by Gardner bubble tube measurements, the polymerization was terminated by the rapid addition of ethanol. The block copolymer was isolated by precipitation into water, washed with water and methanol, and dried to a constant weight of 1500 g. Polymerization results are summarized in Table IV.

Molding and Testing of Block Copolymers

The granular block copolymers were mixed with 3 wt % Thermolite 13 heat stabilizer and milled into coarse sheets at 100°C on a two-roll mill. The coarse sheets were then preheated on a press for 5 min and compression molded at 170°C and 415 MPa. The resulting smooth 150 mm × 150 mm × 1.2 mm sheets were cut into pieces and tested according to ASTM D638-76, D1004-66, D1043-72, and D2240-75. The mechanical properties are summarized in Table V.

RESULTS AND DISCUSSION

Effect of Solvent on Ozonization

The ozonization of commercial suspension grade poly(vinyl chloride) with a molecular weight of 51,000 proceeded very well in 1,1,2,2-tetrachloroethane, as reported by Michel.⁶ However because of the high toxicity of this solvent and the large quantities that would be used in this work, several other chlorinated solvents, including four aliphatic and one aromatic, were investigated. In each case a 5-wt % solution of PVC was used and the ozone generation was kept constant. In these chlorinated solvents the reaction medium began as a suspension, changed to a swollen gel, and with continued heating and ozonization, progressed to a clear solution. The time required for complete solubility varied from 4 h with 1,1,2,2-tetrachloroethane to 20 h with 1,1,1-trichloroethane. Samples were taken at 2 h intervals, the solvent was removed by flash evaporation, and solution

TABLE V
Mechanical Properties of Block Copolymers

Polymer	Tensile strength (MPa)	100% modulus (MPa)	Ultimate elongation (%)	Tear strength (kN/m)	Shore D hardness	Torsional stiffness temperature (°C)
PVC-PPO-1	7.8	7.6	147	48.3	38	-5
PVC-PPO-2	8.9	8.4	155	50.3	36	-4
PVC-PTMA-1	31.5	22.7	195	108.5	52	25
PVC-PTMA-2	21.0	18.7	215	98.0	48	22
PVC-PTMO-1	10.6	10.3	180	67.8	43	-18
PVC-PTMO-2	9.9	8.9	193	60.0	42	-22
PVC-PTMO-3	30.4	20.6	125	75.1	85	25
PVC-PCL-1	25.3	4.5	420	45.0	35	-1
PVC-PCL-2	15.6	1.7	610	27.3	20	-10

viscosities were determined in tetrahydrofuran at 30°C. Figure 1 shows the change in inherent viscosity as a function of time for the various solvents at different temperatures. Even though some of the ozonizations were carried out at higher temperatures, a factor that should increase ozonization efficiency, 1,1,2,2-tetrachloroethane at 70°C was the most efficient solvent.

The goal in each case was an inherent viscosity of 0.10 since this was found to correspond with an acid-terminated poly(vinyl chloride) molecular weight of about 3000. In 1,1,1-trichloroethane at 80°C the molecular weight was still 15,600 after 24 hours (see Table I). After 20 h in chloroform at 60°C the molecular weight was still 7300 and 28 h were required in *o*-dichlorobenzene at 100°C to reduce the molecular weight to 3700. Only 1,2-dichloroethane approached the best solvent in efficiency. The observed differences in efficiency of ozonization could be due to factors that have not been studied, such as, solubility of the early ozonization products and solubility of ozone in the reaction mixture. Qualitative observation of how fast the reaction mixture becomes a solution agrees with the viscosity results. As a compromise between toxicity of solvent and speed of reaction 1,2-dichloroethane was used in the preparation of carboxy terminated poly(vinyl chlorides) described here.

Functionally Terminated Poly(vinyl Chloride)

The carboxy terminated poly(vinyl chlorides) obtained were fine powders with a white to slightly yellow coloration. Four polymers were made, as shown in Table II, by controlling the ozone generation and reaction time. The discrepancy

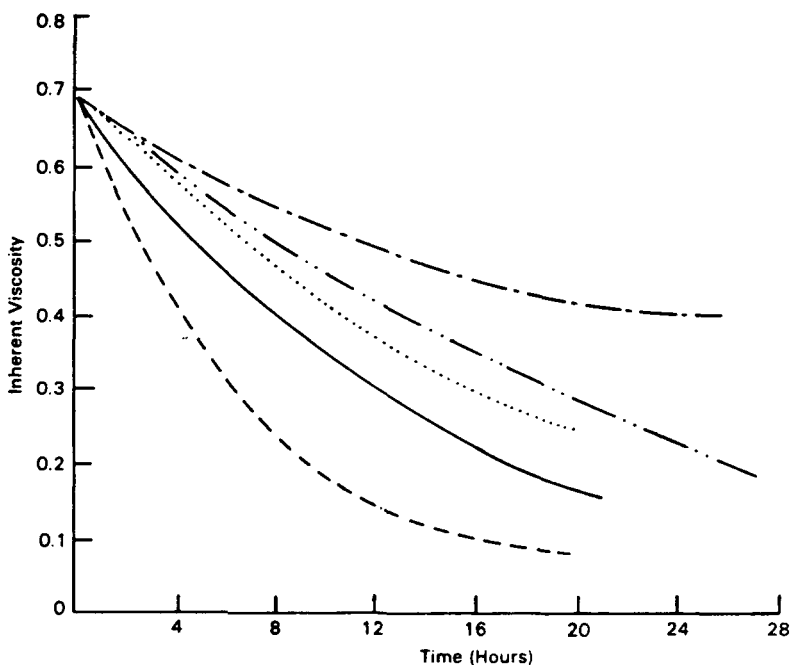


Fig. 1. Inherent viscosity vs. time during the ozonization of PVC in chlorinated solvents. (---) 1,1,1-trichloroethane (80°C); (-.-.-) chloroform (60°C); (.....) *o*-dichlorobenzene (100°C); (—) 1,2-dichloroethane (70°C); (- - -) 1,1,2,2-tetrachloroethane (70°C).

in reaction times between Tables I and II was due to the much larger scale of reactions reported in Table II and subsequent less efficient use of ozone. Excellent yields in the range of 80–85% and functionalities of 1.7–1.9 as determined from acid numbers and number average molecular weight were obtained. With the exception of a very strong carbonyl maximum at 1735 cm^{-1} the infrared spectra were indistinguishable from poly(vinyl chloride). The proton nuclear magnetic resonance spectrum was also undistinguished. The presence of unstable peroxides was indicated by the instability of these low molecular weight polymers at room temperature. Samples allowed to stand for several weeks became very dark grey in color and evolved a strong hydrochloric acid odor.

Several reducing agents, including 1,4-diborane, lithium aluminum hydride, sodium diethylhydroaluminum, sodium bis(2-methoxyethoxy) aluminum hydride, and diisobutyl aluminum hydride were investigated for converting the polymer acid end groups to hydroxyls. Because of the basicities of some of these reducing agents, dehydrochlorination and subsequent yellowing of the polymer took place. The most efficient agent with respect to completion of reaction and work up proved to be lithium aluminum hydride. Although this hydride can dehydrohalogenate poly(vinyl chloride) at elevated temperatures,⁹ reductions conducted at room temperature as shown in Table III did not result in significant loss of hydrogen chloride. The molecular weights of the hydroxy terminated polymers were essentially the same, within experimental error, as the starting materials. Infrared spectroscopy showed complete reduction as the infrared maximum at 1735 cm^{-1} disappeared. The only new maximum, indicative of the hydroxy end groups, was observed in the range of $3500\text{--}3300\text{ cm}^{-1}$. The proton nuclear magnetic resonance spectrum showed the usual singlet at $4.4\ \delta$ and multiplet from 1.8 to $2.3\ \delta$ as well as a broad maximum from 3.6 to $3.9\ \delta$ which is attributable to the methylene protons of the $-\text{CH}_2\text{OH}$ and $-\text{CH}_2\text{CH}_2\text{OH}$ end groups. Unlike the acid terminated poly(vinyl chlorides) these white polymers could be stored indefinitely at room temperature without decomposition since any peroxides formed during organization would have been removed during the reduction stage. Attempts to determine accurate hydroxyl numbers were not successful due to the susceptibility of the low molecular weight polymers to dehydrochlorinate in the presence of heat and basic conditions required in the standard method of analysis.¹⁰ Reproducible values were also not obtained when modified determinations were carried out at room temperature. Functionality was thus assumed to be the same as the original carboxy terminated polymers.

(AB)_x Block Copolymers

The block copolymers were prepared in a two-step sequence. The polyether or polyester diol was first capped with a diisocyanate such as methylene-bis(4-phenylisocyanate)(MDI), methylene-bis(4-cyclohexylisocyanate)(MDCI), or toluene diisocyanate (TDI). The extent of capping was determined by isocyanate analysis¹¹ with results as shown in Table IV. The isocyanate-capped polyol was then condensed directly with hydroxy-terminated poly(vinyl chloride). The reaction sequences are indicated below, with MDI and poly(tetramethylene

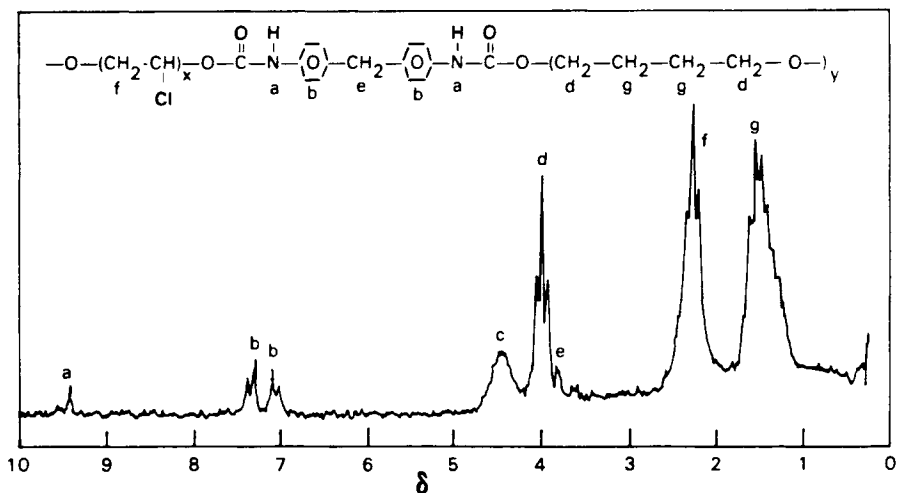
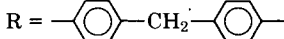
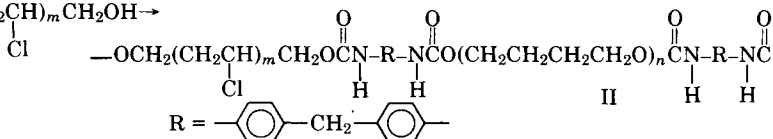
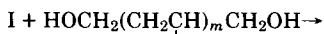
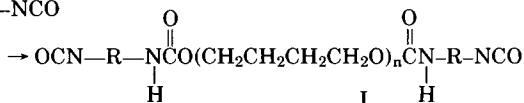
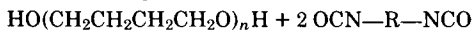


Fig. 2. Proton nuclear magnetic resonance spectrum of PVC-PTMO block copolymer.

oxide) being used as examples:



Dibutyltin dilaurate and triethylene diamine were used as catalysts. In the initial polymerizations the reaction was terminated when the infrared spectrum did not show an isocyanate maximum at 2260 cm^{-1} . However, before the isocyanate maximum completely disappeared, crosslinking resulted with some polymers due to isocyanate reactions with secondary hydroxy groups on the PVC chain or due to the formation of allophanate linkages. The polymerizations were subsequently carried out with less catalyst and the solution viscosity was monitored so that when a very large increase in viscosity was observed, the polymerization could be terminated and crosslinking avoided. As shown in Table IV several different block copolymers were synthesized with hydroxy terminated poly(vinyl chlorides) of either 3000 or 4300 molecular weight. The poly(vinyl chloride)-*b*-poly(tetramethylene oxide) (PVC-PTMO) block copolymers were synthesized with MDI, MDCl, and TDI as coupling agents. Number average molecular weights were between 21,000 and 23,000, which defined a repeat unit of about 10 blocks. The wt % polyol in the block copolymer as determined by elemental analysis was lower than that calculated for a pure (AB)_x polymer and indicated that the end blocks were poly(vinyl chloride). The infrared spectrum contained the expected maximum at 1745 cm^{-1} due to the urethane linkage. Figure 2 is a representation of the proton nuclear magnetic resonance (PNMR) spectrum of a PVC-PTMO block copolymer in dimethyl sulfoxide-*d*₆. The peak assignments have been made based on PNMR spectroscopy of the starting materials. Poly(vinyl chloride)-*b*-poly(tetramethylene adipate) (PVC-PTMA)

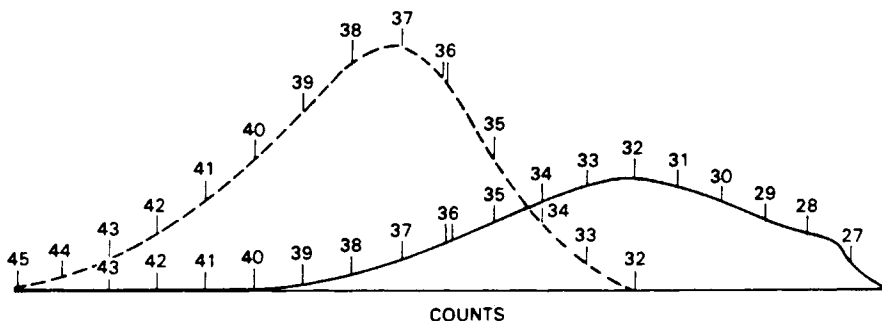


Fig. 3. Gel permeation chromatography (GPC) curves of hydroxy terminated PVC H-15 (---) and PVC-PTMA (AB)_x block copolymer (—).

copolymers were also synthesized but with higher molecular weights. The molecular weight distributions, as shown in Figure 3, were not narrow. The gel permeation chromatogram for the starting hydroxy terminated PVC is shown for comparison. High molecular weight poly(vinyl chloride)-*b*-poly(propylene oxide) (PVC-PPO) and poly(vinyl chloride)-*b*-polycaprolactone (PVC-PCL) copolymers were also synthesized. These copolymers contained between 32 and 44 wt % of the respective polyol and yielded the expected infrared and PNMR spectra. The polymers were all white polymers and yielded clear flexible films when cast from solution.

Differential scanning calorimetry (DSC) indicated two glass transition temperatures for the poly(vinyl chloride)-*b*-poly(tetramethylene oxide) and poly(vinyl chloride)-*b*-poly(tetramethylene adipate) copolymers as shown in Figure 4. Thus, at least at this concentration of polyol, the polymer segments are incompatible. The poly(vinyl chloride)-*b*-polycaprolactone copolymers exhibited only one T_g at 0°C, midway between the T_g 's of the respective homopolymers. This compatibility is not unexpected from analogy with blends of these two polymers.¹² Differential scanning calorimetry of compression molded PVC-PCL

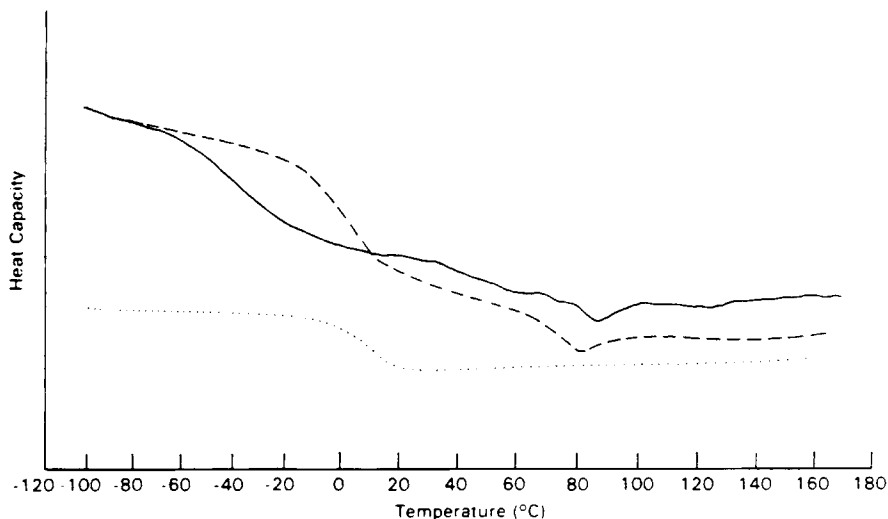


Fig. 4. Differential scanning calorimetry curves of PVC-PTMO-1 (—), PVC-PTMA-2 (---), and PVC-PCL-2 (.....).

copolymers, however, showed a very small endotherm at 44°C due to the melting of crystalline polycaprolactone segments. Standing at room temperature for 4 weeks and repeating the DSC showed a pronounced melting endotherm indicating increased crystallization. Apparently the quenching involved in compression molding induced crystallization of the polycaprolactone segments.

The various block copolymers exhibited a range of mechanical properties, as shown in Table V. The PVC-PPO copolymers had torsional stiffness temperatures (T_f) slightly below 0°C but also had low tensile strengths. The other block copolymers had higher tensile strengths, with PVC-PTMA-1 having the highest. The torsional stiffness was controlled more by the type of polyol used than by the amount. For example, comparing the four block copolymers PVC-PTMA-2, PVC-PTMO-1, PVC-PTMO-2, and PVC-PCL-2 which contained 41–44 wt % polyol. The poly(tetramethylene adipate) based block copolymer had a T_f temperature of 22°C and the polycaprolactone containing copolymer had a T_f temperature of -10°C. Poly(tetramethylene oxide) proved to be the most efficient flexibilizer since the PVC-PTMO copolymers had very low temperatures of -18°C and -22°C. Only the poly(vinyl chloride)-*b*-polycaprolactone copolymers achieved high tensile strengths in the range 15–25 MPa together with low torsional stiffnesses as well as very high elongations of 420–610%. A comparison of mechanical properties within a particular series, e.g., PVC-PTMO, shows the effect of relative copolymer backbone flexibility. Increasing the polyol content from 24% to 43% and changing the diisocyanate coupling agent from the rigid toluene diisocyanate to the more flexible methylene-bis(phenylisocyanate) or methylene-bis(4-cyclohexylisocyanate) greatly reduced the T_f temperature. These materials have torsional stiffnesses achievable with the poly(vinyl chloride) homopolymer only by means of the addition of large amounts of plasticizer, i.e., 40 phr dioctylphthalate.³ Similarly, with the poly(vinyl chloride)-*b*-polycaprolactone copolymers an increase in flexible unit content increased the flexibility of the copolymer as evidenced by a lowering of the T_f temperature. When compression molded, the PVC-PCL copolymers were initially very flexible. On standing at room temperature, however, the plaques noticeably hardened. This was due to crystallization of the polycaprolactone segments described earlier with the DSC results.

As shown by the research reported here, poly(vinyl chloride) can be internally plasticized. Through the correct choice of polyol and coupling agent, block copolymers with excellent low temperature flexibilities and mechanical properties can be obtained.

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