

Block Copolymers of Polycarbonates with Several Hydroxy-Terminated Elastomers to Yield Thermoplastic Elastomers for Higher Service Temperature

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Synopsis

The synthesis of block copolymers and the study of their morphology were undertaken to find improved thermoplastic rubbers for service at elevated temperatures. The basis was the extraordinary properties possessed by ABA-type block copolymers in which the terminal blocks are polystyrene and the central block is either polyisoprene or polybutadiene. In these systems it has been well established that the unusual properties are a result of domain formation in which the hard and the soft blocks aggregate separately into distinct phases. The hard segment is thought to act both as a crosslink and as a filler. Block copolymers were synthesized with different soft and hard segments. The effects of these segments and of their properties on the morphology and the stress-strain properties of the block copolymers were measured and evaluated. Electron microscopy and birefringence were used to determine the morphology. It was found that the glass transition temperatures of the segments, the bulk of the monomer unit in the glassy segment, and the morphology determined the strength of the material. Some of the materials prepared have tensile strengths of 0.1 kg/cm² or more at temperatures in excess of 180°C and therefore appear promising as elastomers for service at elevated temperatures.

INTRODUCTION

Elastomeric materials can be reversibly deformed by the application of stress. This property is a result of virtually unrestricted segmental mobility in the polymer chains. This unimpeded motion on the chain segments is only restricted by occasional tie-down points within the elastomer matrix. Tie-down points, which until recently were believed to be in the form of covalent and ionic crosslinks, hydrogen bonding, or crystallinity, have been considered to be one of the basic molecular requirements for an elastomer.

The mechanical properties of high polymers are determined primarily by the transitions and the temperatures at which they occur. The materials with high glass transition temperatures have higher failure temperatures, but at the same time they are tough, often brittle materials at room temperature. The failure temperature of an elastomer can be raised,

without completely destroying its low temperature flexibility, by blending it with a suitable plastic having a high glass transition temperature. The plastic reinforces the rubber phase.

In recent years, considerable attention has been given to ABA-type block copolymers in which the terminal blocks are polystyrene and the central block is either polyisoprene or polybutadiene.¹⁻³ The "hard" (polystyrene) and "soft" (polybutadiene) blocks are thought to aggregate into distinct and separate phases. The plastic phase in these two-phase systems acts both as a crosslink and as a filler.⁴ The separation of the phases and accompanying reinforcement occurs only when the blocks are incompatible, with the terminal "hard" blocks remaining rigid up to temperatures well in excess of service temperatures.

Several block copolymers based on bisphenols have been prepared and studied by previous workers.⁵⁻⁹ The polycarbonate elastomers prepared by these workers were not chemically crosslinked, contained no hydrogen bonding, and the materials prepared by Caldwell et al.⁸ were shown by x-ray diffraction studies to be noncrystalline. These elastomers contained bulky three-dimensional polycyclic groups which contributed to the properties of the elastomer by acting as tie-down points. It was shown that in order to produce an elastomer with a useful temperature range, the hard segments must have a high softening temperature to counteract the lower glass transition temperature of the soft segment.

In this study, a series of block copolymers were prepared, the glassy phases of which were polycarbonates of several aromatic and alicyclic diols. Polybutadiene, poly(ethylene adipate), and butanediol polycarbonate were used for the "soft" segments of the elastomers. The purpose was to study the improvement in the service temperatures of these elastomers and the factors affecting the increased thermal resistance. It was hoped that the higher glass transition temperatures of the plastic phase would result in an increase in the service temperature, whereas the proper selection of the rubber phase would give better properties at low temperatures, thus increasing the useful temperature range of these materials.

Preliminary studies¹⁰ showed that such a block copolymer could be made by forming bisphenol A polycarbonate blocks on either hydroxy-terminated polybutadiene (R-45M, Sinclair Petrochemicals Inc.) or hydroxy-terminated polyester (Multrathane-R14, Mobay Chemical Co.). The encouraging results were that in each case as the temperature was raised the elongation at break increased and the load bearing capacity increased so that the polymers were still highly elastic at 180°C, much above the temperatures for the corresponding diisocyanate-cured elastomers.

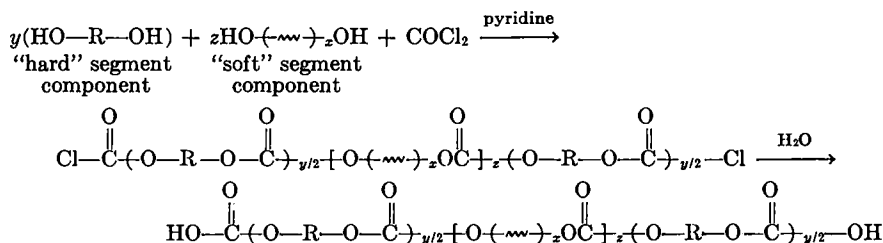
EXPERIMENTAL

Polymers

For convenience, the elastomers prepared in this study will be designated by a three-sequence code such as ES-35-1. ES, PB, and BU refer to the

soft segments poly(ethylene adipate), polybutadiene, and butanediol polycarbonate. The polycarbonate segments derived from bisphenol A, 4,4'-cyclohexyldenediphenol, phenolphthalein, 1,4-cyclohexanediol, and 2,2,4,4-tetramethyl-1,3-cyclobutanediol will be referred to by numbers 1, 2, 3, 4, and 5, respectively, and the middle number, 35, refers to the weight per cent of the "hard" segment. The elastomers prepared are listed in Table I.

The polycarbonate elastomers were prepared using the method described by Caldwell et al.⁸ When alicyclic diols were used for the "hard" segments, few modifications were made in the method of preparation. The reactants in the required proportions were dissolved in 100 ml toluene, and twice the calculated amount (molar basis) of pyridine was added. This solution was refluxed under nitrogen for 5 min. The addition of phosgene was as follows: 66% of phosgene at the rate of 1 ml/min at 45°C; 34% of phosgene at the rate of 1 ml/min at 75°C; and 25% molar excess of phosgene at the rate of 1 ml/5 min at 85°C. The product solution was washed with water, dilute hydrochloric acid, and water, and the product was precipitated in methanol. The reaction can be written as follows:



where the "hard" segment component, HO—R—OH, may be an aromatic or an alicyclic diol.

Isothermal Stress-Strain and Birefringence Measurements

The elastomers were chain extended with tolylene diisocyanate (TDI) and an antioxidant was added. The samples were prepared by casting dilute methylene chloride-polymer solutions onto clean mercury surfaces. Birefringence was measured with the compensation technique.¹¹ To obtain elongation, the distance between two parallel marks on the film was measured simultaneously with a precision cathetometer. The measurements were carried out in a double-walled glass chamber kept at the desired temperature within $\pm 0.5^\circ\text{C}$ by circulating thermostated oil.

The experimental procedure was as follows: After thermal equilibration and recording of the distance between the fiduciary marks on the specimen, a load was applied to the lower free clamp attached to the rubber strip. The rate of loading was kept constant in all experiments at 5 g/min. The compensator reading, elongation, and the load were recorded. Measurements were continued until the sample started to elongate at the rate of 1 cm/min. In some cases, the sample broke before this state was reached.

TABLE I
Structure of Block Copolymers

Elastomer	Soft segment	Hard segment, wt-%	Hard segment monomer	Inherent viscosity before chain extension with TDI
PB-40-1	polybutadiene	40	bisphenol A	0.75
PB-35-1	polybutadiene	35	bisphenol A	0.68
BU-40-1	butanediol polycarbonate	40	bisphenol A	0.44
BU-35-1	butanediol polycarbonate	35	bisphenol A	0.55
ES-40-1	poly(ethyleneadipate)	40	bisphenol A	1.2
ES-35-2	poly(ethyleneadipate)	35	cyclohexylidenediphenol	1.23
ES-40-3	poly(ethyleneadipate)	40	phenolphthalein	0.81
ES-35-3	poly(ethyleneadipate)	35	phenolphthalein	0.82
ES-40-4	poly(ethyleneadipate)	40	cyclohexanediol	0.51
ES-40-5	poly(ethyleneadipate)	40	tetramethylcyclobutenediol	0.60

The applied stress at this point was considered to be the tensile strength. The other two dimensions of the specimen at any time during the experiment were calculated from the initial dimensions and the elongation at that time, and assuming constant volume deformation. At temperatures above 50°C, the thermostated chamber was kept filled with dry, oxygen-free nitrogen.

Differential Scanning Calorimetry (DSC)

DSC measurements were made on the solution-cast samples of polycarbonate elastomers using a du Pont Model 990 thermal analyzer with DSC accessory.

Microscopy

A Phillips EM300 electron microscope with a goniometer stage was used for obtaining microphotographs of thin films of polycarbonate elastomers containing polybutadiene.

RESULTS

NMR Results

The nuclear magnetic resonance traces of the polycarbonate elastomers based on aromatic diols show that the ratios of the number of aromatic

hydrogen atoms to the number of aliphatic hydrogen atoms derived from the "soft" segments are the same as the ratios of the reactants used in the preparation of these materials.

Stress-Strain Birefringence Results

Figures 1 and 2 show the stress-strain behavior of PB-40-1 at different temperatures. The data are plotted in the form of true stress against $\lambda^2 - (1/\lambda)$, where λ is the extension ratio. These curves can be divided into three regions: the high-modulus region I, yielding followed by region II, and finally high-modulus region III. Region III is not very pronounced in the data at higher temperatures. The increase in temperature results in large decreases in the modulus and tensile strength. The measured values of Young's modulus are listed in Table II. The stress-birefringence be-

TABLE II
The Stress-Optical and Stress-Strain Data for the Copolymers PB-40-1 and PB-35-1

Sample	Temp., °C	$\Delta n/t$, cm ² /kg × 10 ⁶	Maximum value obtained × 10 ⁶	$C_h V_h$ × 10 ⁶	$C_s V_s$ × 10 ⁶	Young's modulus, dynes/cm ² × 10 ⁻⁶
PB-40-1	25	1.5	4.9	0.14	23.1	78.9
	55	2.1	9.54	—	—	35.0
	110	24.0	43.7	—	—	5.2
	130	40.9	54.7	—	—	3.2
	160	28.1	53.1	—	—	1.7
PB-35-1	25	8.1	9.1	0.12	25.1	22.0
	55	10.3	17.2	—	—	10.9
	110	49.7	51.5	—	—	4.8
	130	31.9	39.0	0.522	—	2.0

havior of PB-40-1 at different temperatures is illustrated in Figures 3 and 4. The initial slope of the stress-birefringence curve is called the stress optical coefficient. In these plots, again three regions are observed. In region I, the increase in birefringence with increasing stress was small, while it became large in region II, and smaller again in region III. The maximum value of the slope is observed at the transition between region II and region III. The stress-optical coefficients and the maximum values of the slopes are listed in Table II. Stress-strain and stress-birefringence data for PB-35-1 follow the same trend and are listed in Table II.

The stress-strain and stress-optical properties of BU-40-1 and BU-35-1 are summarized in Table III. These materials are weaker than the materials containing polybutadiene as the soft segment. The initial high-modulus region of stress-strain curves is followed by rapid increase in elongation with stress which is followed by failure. In the stress-birefringence plots, region II is not observed.

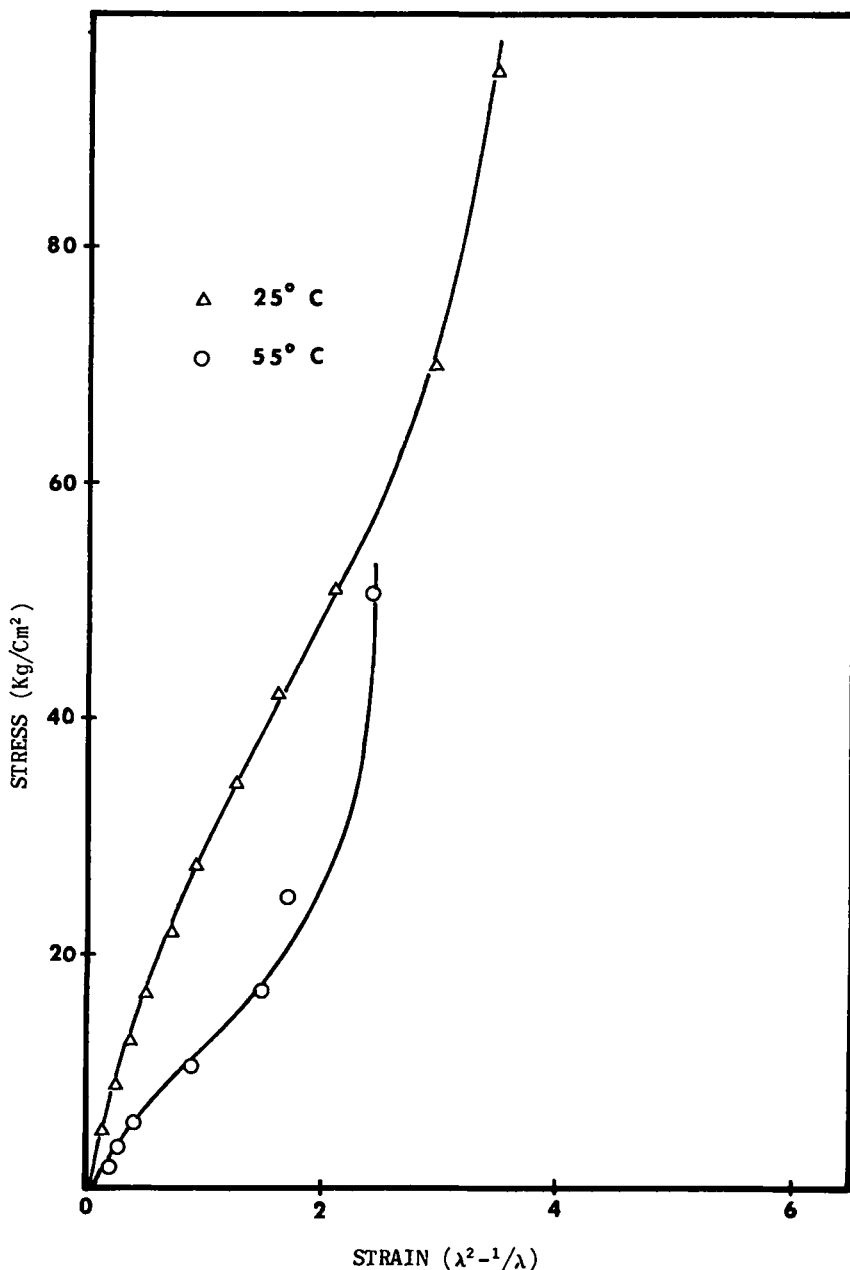


Fig. 1. Stress-strain data for polybutadiene/bisphenol A polycarbonate block copolymer, 60/40 weight ratio, at lower temperatures.

Table IV contains the stress-strain and stress-optical data for ES-40-1, ES-35-2, ES-35-3, and ES-40-3. Region III in the stress-strain curves is not very pronounced. There are small differences between the stress-optical coefficients and the maximum value of the slopes of stress-birefringence curves.

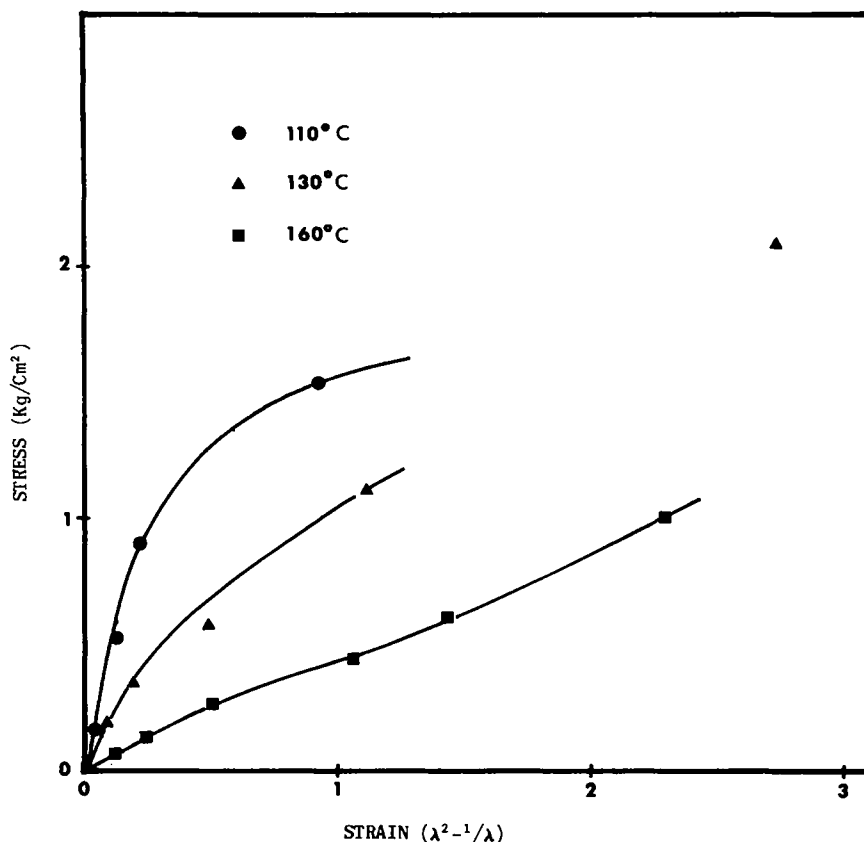


Fig. 2. Stress-strain data for polybutadiene/bisphenol A polycarbonate block copolymer, 60/40 weight ratio, at higher temperatures.

The stress-strain and stress-optical data for ES-40-4 and ES-40-5 exhibit the pattern observed for PB-40-1. These data are also listed in Table IV.

DISCUSSION

The stress-strain and stress-optical data of PB-35-1 and PB-40-1 (Table II) can be explained as a result of the separation of bisphenol A polycarbonate and polybutadiene phases. The initial high modulus arises from the interconnected bisphenol A polycarbonate phase (incomplete phase separation) embedded in the continuous polybutadiene phase. Yielding is accompanied by breaking up of the network of the plastic phase with the polybutadiene phase supporting increasing amounts of the load. The yield point is followed by a high-modulus region, and this upturn in the stress-strain curve at large elongations may be due to either crystallization induced by molecular orientation or non-Gaussian behavior of chain segments stretched to near-maximum length.^{11,12} Systems such as the ones investigated in this study were found to be noncrystalline.⁸ The two-phase system proposed and the stress redistribution between the phases is

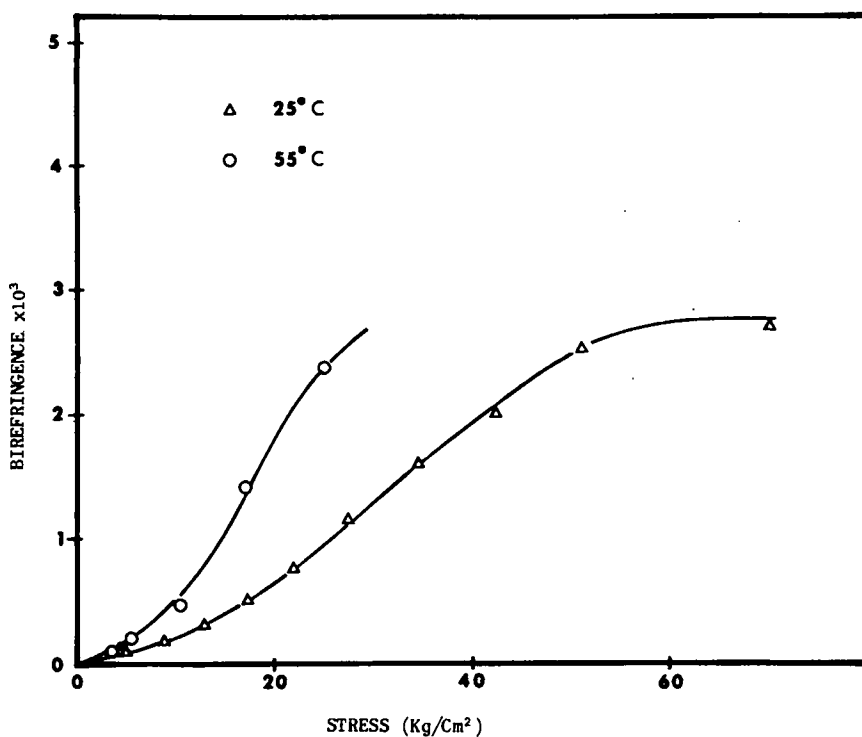


Fig. 3. Stress-birefringence data for polybutadiene/bisphenol A polycarbonate block copolymer, 60/40 weight ratio, at lower temperatures.

supported by the stress-optical data. By assuming that the anisotropy of each phase is an additive property and that the stress-optical coefficient for each block is the same as it is for the homopolymer, an equation for the stress-optical coefficient of the copolymers can be derived:^{1,13}

$$C = \Delta n/t = C_n V_n (t_n/t) + C_s V_s (t_s/t). \quad (1)$$

Thus, the changes in the ratio of birefringence to stress can be accounted for by postulating changes in the distribution of stress between the two

TABLE III
The Stress-Optical and Stress-Strain Data for Copolymers BU-40-1 and BU-35-1

Sample	Temp., °C	$\Delta n/t$, cm ² /kg $\times 10^5$	Maximum value observed $\times 10^5$	Young's modulus, dynes/cm ² $\times 10^{-6}$
BU-40-1	25	50.7	50.7	20.0
	30	50.7	50.7	4.6
	40	49.1	49.1	1.4
	50	47.0	47.0	0.6
BU-35-1	25	55.4	55.4	18.3
	30	40.4	40.4	6.1
	40	35.2	35.2	3.2
	50	—	—	0.6

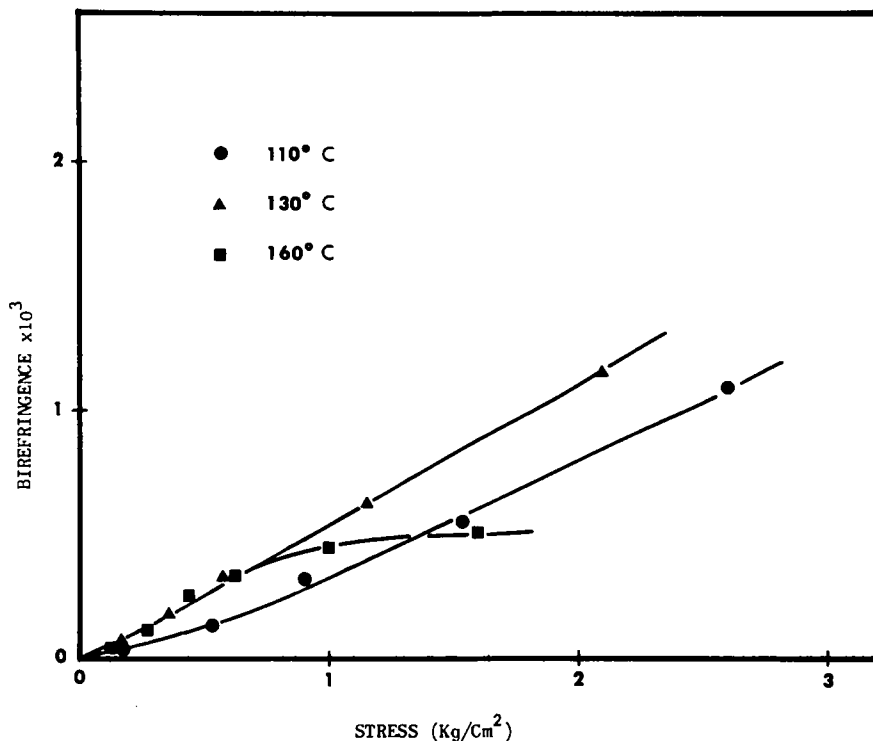


Fig. 4. Stress-birefringence data for polybutadiene/bisphenol A polycarbonate block copolymer, 60/40 weight ratio, at higher temperatures.

phases. Table II contains the approximate values of $C_h V_h$ and $C_s V_s$, which would have been observed as the stress-optical coefficient of the system had the load been borne entirely by bisphenol A polycarbonate or by polybutadiene. These values indicate that initially the plastic phase carries a major part of the load. Using eq. (1), the percentage of stress carried by the plastic phase can be determined. The value is 68% for PB-35-1 and 94% for PB-40-1. The phase separation in PB-35-1 and PB-40-1 was confirmed by electron photomicrography. Thin films were cast directly from a dilute methylene chloride solution on the copper grid placed on a flat Teflon surface. Osmium tetroxide solution (1%) was used for staining the films. The increased contrast results from OsO_4 adding onto the double bonds in polybutadiene. Figure 5 shows the electron photomicrograph of PB-35-1 film.

The stress-optical coefficient of the copolymers increases with increasing temperature except at temperatures approaching the glass transition temperature of the plastic phase and above it. This results from (i) increasing amount of the load being transferred to the polybutadiene continuous phase and (ii) higher stress-optical coefficient of polybutadiene due to increased uncoiling of the chains. At the temperature approaching the glass transition temperature of bisphenol A polycarbonate and rising above it, the

TABLE IV
The Stress-Optical and Stress-Strain Data for Copolymers
ES-40-1, ES-35-2, ES-35-3, ES-40-3, ES-40-4, and ES-40-5

Sample	Temp., °C	$\Delta n/t$, cm ² /kg $\times 10^5$	Maximum value observed $\times 10^5$	Young's modulus, dynes/cm ² $\times 10^{-6}$
ES-40-1	25	40.5	44.0	6.1
	35	22.5	26.4	4.1
	45	—	—	0.62
ES-35-2	25	2.67	2.67	11.3
	40	33.3	33.3	6.5
	50	56.3	56.3	2.2
ES-35-3	25	5.2	11.5	47.4
	45	7.2	14.1	6.5
	55	10.3	12.0	1.8
	75	19.7	—	1.0
ES-40-3	25	4.8	8.4	32.1
	45	8.3	9.2	14.1
	55	6.1	7.2	5.9
	75	16.1	—	1.5
ES-40-4	25	0.23	6.1	78.3
	50	0.22	—	17.6
	70	—	—	10.5
	110	—	—	3.8
	130	—	—	2.8
	160	—	—	0.7
	ES-40-5	25	—	—
	55	—	—	27.6
	110	—	—	9.5
	130	—	—	5.7
	160	—	—	3.5

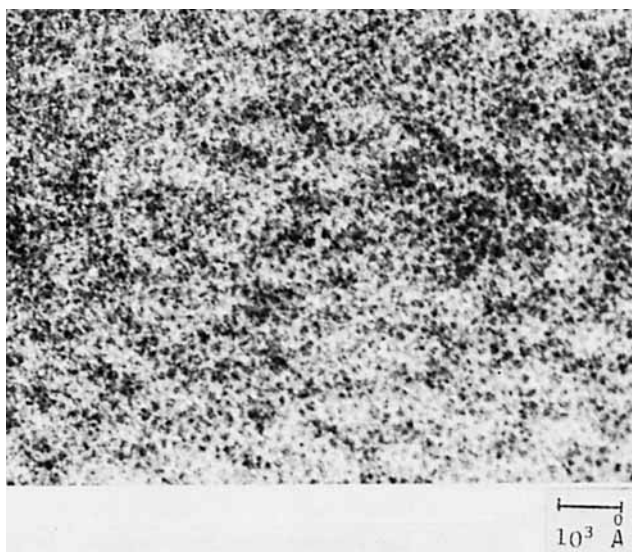


Fig. 5. Photomicrograph of section of film of polymer PB-35-1.

crosslinking provided by the plastic phase is not as effective, giving rise to increased tendency to flow and to a decrease in stress-optical coefficient.

The materials BU-35-1 and BU-40-1 behave as lightly crosslinked rubbers. The overall strength of these materials results from butanediol polycarbonate, whereas the bisphenol A polycarbonate phase forms physical crosslinks and acts as a filler. The stress-optical data indicate that phase separation is complete. The initial slope of the stress-birefringence curve is the maximum value of the stress-optical coefficient observed, suggesting that from the start of the deforming process the butanediol polycarbonate phase supports most of the load with no subsequent redistribution of the stress. Since the plastic phase does not directly take part in the load-supporting function (providing reinforcing effects only as a filler and tie-down points), these materials are generally weak and cannot withstand elevated temperatures. The decay of birefringence with increasing temperature results from the slippage of the butanediol polycarbonate chains because the plastic phase (bisphenol A polycarbonate) is not very effective as tie-down points.⁸

The material ES-40-1 behaves as a crosslinked rubber in which bisphenol A polycarbonate phase acts as crosslinks and as a filler and takes a small part in the load-bearing function. There are small differences between the stress-optical coefficients and the maximum values of the slopes of birefringence stress curves. The phase separation is not complete, and in the initial stages of the deformation process the plastic phase supports a significant part of the load. Stress redistribution between the phases takes place as stress increases.

The stress-strain and stress-optical data for ES-35-2 suggest that cyclohexylidenediphenol polycarbonate provides more effective physical crosslinking. This is also shown by other authors.⁷ The birefringence does not decrease with increasing temperature because the poly(ethyleneadipate) chains are prevented from slipping past each other. The increase in birefringence with increasing temperature results from increased uncoiling of the chains. The phase separation is complete as indicated by the absence of stress redistribution between the phases.

Phenolphthalein polycarbonate as the plastic phase in ES-35-3 and ES-40-3 provides increased reinforcement as tie-down points and as a filler. The phase separation is not complete and the plastic phase takes a direct part in the load-supporting function. Stress redistribution takes place as stress increases. This is suggested by the stress-optical data. The materials, therefore, are quite strong and can withstand higher temperatures. Because of more effective physical crosslinks provided by the plastic phase the slippage of poly(ethyleneadipate) chains, as indicated by a decrease in birefringence with increasing temperature, is not observed.

The stress-strain curves for ES-40-40 and ES-40-5 can be divided into three parts: (i) high-modulus region, (ii) low-modulus region followed by yielding, and (iii) upturn at large elongations. The high modulus results from the continuous network of interconnected domains of the plastic

phase (cyclohexanediol polycarbonate or tetramethylcyclobutanediol polycarbonate) supporting almost all of the load. As the stress increases, redistribution of stress takes place and the poly(ethyleneadipate) phase takes an increasing share in the load-bearing function. This accounts for the region followed by yielding. The high strength results from the continuous network of interconnected domains of the plastic phase.

The presence of the glassy phase as a continuous network is confirmed by the stress-optical data in the case of ES-40-4. The low stress-optical coefficient results from the glassy phase supporting most of the load up to 35 kg/cm². The sudden increase in the slope of the stress-birefringence curve results from the transfer of load from the "hard" segment to the rubber.

In the foregoing, the stress-strain properties of the materials prepared were explained on the basis of phase separation. The materials ES-40-1, ES-35-3, and ES-40-3 consist of a poly(ethyleneadipate) continuous phase interspersed with domains of plastic phase with a small number of interconnecting strands (incomplete separation of phases). The high-modulus portions of the stress-strain curves result from the glassy phase supporting a substantial part of the load. At higher stresses, the glassy phase pulls apart and the stress redistribution results in lower modulus. In BU-35-1 and BU-40-1 and ES-35-2, the phase separation is complete and the domains of the glassy phase act as inert filler and physical crosslinks. The reinforcing effect is minimal and the materials are weak. The plastic phase in PB-40-1 and PB-35-1 consists of highly interconnected paths of bisphenol A polycarbonate. This accounts for these being high-strength materials. Incomplete phase separation in ES-40-4 and ES-40-5 results in the domains of the glassy phase embedded in the rubbery continuous phase. These domains are interconnected and are large in size.

The effect of temperature is twofold in such a unique system. As the "soft" segment phase is heated, it loses strength and tends to flow readily. It is restrained until the plastic phase reaches a condition in which the blocks of the plastic phase can pull out of the glassy domains and allow the rubber phase to flow. The glass transition temperature of the glassy phase should therefore be much higher than the service temperature of the block copolymer. The glassy phase above its glass transition temperature acts as an elastic liquid and therefore cannot be effective as physical crosslinks. The reinforcing mechanism breaks down.

The limits to the operating temperatures of these copolymers are largely set by the glass transition temperature and hence the flow properties of the plastic phases. The available glass transition data are presented in Table V. These data indicate that it is possible to prepare block copolymers with various glassy plastics with higher glass transition temperatures and to successfully raise the operating temperatures.

The morphology of a block copolymer plays a major role in determining the tensile strength of the material at elevated temperatures. The separation of the blocks into two distinct phases, in which the plastic phase forms

either a network of interconnected domains embedded in the continuous phase formed by the rubber or the plastic phase forms the continuous phase, results in stronger products.^{1,13,14} The products will be elastomer-toughened plastic which have yield points and, thereafter, are typically thermoplastic, i.e., the rubbery blocks anchored in at least two glassy domains. The morphology of such materials depends greatly on the solvent used for casting. When the samples were cast from solvents for the plastic phase, the material had a glassy continuous phase.

Occasional chemical crosslinks introduced into the rubber phase will result in an increase in the total number of crosslinks and will give rise to a tougher material.

TABLE V
Summary of Data for the Block Copolymers Listed in Table I^a

Sample	Hard segment T_g , °C	Soft segment		Temperature at which the applied stress at break is 0.1 kg/cm ² , °C	Young's modulus, dynes/cm ² × 10 ⁶
		T_g , °C	T_m , °C		
ES-40-1	142, ^b 149 ^c	-39 ^b	50	57	6.17
BU-35-1	142 ^b	—	—	58	18.3
BU-40-1	142 ^b	—	—	62	20.
PB-35-1	142 ^b	-76 ^b	64 ^b	186	22.
PB-40-1	142 ^b	-76 ^b	64 ^b	264	78.9
ES-35-2	170 ^b	-39 ^b	50	76	11.3
ES-35-3	244 ^b	-39 ^b	50	80	47.4
ES-40-3	244 ^b	-39 ^b	50	94	32.1
ES-40-4	178 ^b	-39 ^b	50	190	78.3
ES-40-5	176, ^b 160 ^d	-39 ^b	50	456	83.8
Polystyrene	94 ^b				

^a For identification of samples, see experimental section and Table I.

^b Determined by the author

^c Ref. (15)

^d Ref. (16)

The strength properties of the block copolymers prepared and studied are summarized in Table V. The comparison of the block copolymers ES-40-1, BU-40-1, and PB-40-1 shows the effect of the three rubber components used in this study. The thermal data on poly(ethyleneadipate) and polybutadiene were obtained by the DSC method, but similar data on butanediol polycarbonate could not be obtained and were not available in the literature. The large difference between the effect of polybutadiene and the other two rubbery components on the strength properties can be attributed to (i) the higher melting temperature, (ii) the polybutadiene phase may have occasional chemical crosslinks (possibly introduced during the curative process), or (iii) incomplete separation of phases.

The comparison of the hard segments 1, 2, 3, 4, and 5 brings out two points. Firstly, the improved properties as we go from bisphenol A polycarbonate to cyclohexylidenediphenol polycarbonate to phenolphthalein polycarbonate result from the increasing glass transition temperatures below which the flow of the rubber phase is restrained, and from increasing bulk of the monomer unit of the glassy phase, making better tie-down points. Secondly, the effect of the cyclohexanediol polycarbonate and tetramethyl cyclobutanediol polycarbonate in providing extra strength may be due to the formation of a network of highly interconnected domains of the glassy phase (incomplete phase separation). The plots of $\log t_B$ against $1/T$ for the materials studied yielded straight lines. Applied stress at break can be expressed as a function of temperature,

$$t_B = Ae^{E/RT}$$

where A is a constant, the value of which indicates the tensile strength of the material at a very high temperature, and E is the energy of activation. The value of A and E for the materials studied are listed in Table VI.

TABLE VI
Values of A and Energies of Activation E for Block Copolymers^a

Material ^b	A , kg/cm ²	E , kcal/mole
ES-40-1	1.4×10^{-16}	22
BU-35-1	5.0×10^{-19}	26
BU-40-1	1.6×10^{-18}	25
PB-35-1	2.5×10^{-8}	14
PB-40-1	2.1×10^{-8}	9
ES-35-2	6.8×10^{-16}	20
ES-35-3	5.7×10^{-18}	26
ES-40-3	2.8×10^{-16}	24
ES-40-4	3.6×10^{-7}	11
ES-40-5	4.2×10^{-4}	8

^a $t_B = Ae^{E/RT}$.

^b For identification of samples see experimental section and Table I.

Andrade¹⁷ derived the relationship $\eta = Be^{E'/RT}$ between viscosity and the temperature, where E' is the energy of activation of viscous flow. Flory¹⁸ determined that the value of E for several polyesters was approximately 8 kcal/mole. Comparison between the bond energies (83.1 kcal/mole for C—C bond and 84.0 kcal/mole for C—O bond) and the energies of activation listed in Table VI indicates that the process of failure of these materials is a physical one (e.g., viscous flow) rather than a chemical process in which chemical bonds are broken. Higher values of E point to a rapid loss of tensile strength with increase in temperature.

Table V lists the temperatures at which the copolymers studied have a tensile strength of 0.1 kg/cm². Using this criterion, the copolymers can be arranged in the order of decreasing strength: PB-40-1, ES-40-5, ES-40-4, PB-35-1, ES-40-3, ES-35-3, ES-35-2, BU-40-1, BU-35-1, and ES-40-1.

CONCLUSIONS

The present work on the synthesis and the study of the block copolymers based on polycarbonates brings out the effect of the different plastic components, the effect of the rubber components, and the effect of the morphology of the material.

The service temperature of the block copolymers is limited by the glass transition temperature and, therefore, the flow properties of the plastic phase. The rubber phase tends to flow as the temperature is increased. It will be restrained until the plastic phase, which acts as tie-down points, reaches a condition in which the block of the glassy component can pull out of the domains and allow the rubber to flow. The greater bulk of the monomer units in the glassy phase results in an increased ability to form physical crosslinks since it becomes harder for the blocks of the glassy phase to pull out of the domains. The decrease in the mobility of the glassy segments resulting from increased bulk of the monomer units would hinder the separation of the phases and thus forming a material containing interconnected domains. Increasing the glass transition of the glassy phase and increasing the bulk of the monomer unit of the glassy phase will, therefore, result in improved tensile strength at elevated temperatures.

The material ES-35-3 with phenolphthalein polycarbonate ($T_g = 244^\circ\text{C}$) as the glassy component had a higher tensile strength than ES-35-2 with cyclohexylidenediphenol polycarbonate ($T_g = 170^\circ\text{C}$), which was in turn stronger than ES-40-1 with bisphenol A polycarbonate ($T_g = 142^\circ\text{C}$). This also shows the effect of the bulk of the monomer unit in the glassy phase. The glassy phase present as a continuous phase or as interconnected domains will result in improved tensile strength at elevated temperature. The examples are PB-40-1 and PB-35-1, in which bisphenol A polycarbonate forms highly interconnected domains. The solvent has a strong effect on the morphology of the copolymers. Results for the first four materials, PB-40-1, ES-40-5, ES-40-4, and PB-35-1, demonstrate the effect of phase separation in which the hard segments either form the continuous phase or form domains which are interconnected so as to form a network. The results for the materials ES-40-3, ES-35-3, RS-35-2, BU-40-1, BU-35-1, and ES-40-1 point to the effects of the bulk of the monomer unit in the glassy phase.

The microscopic techniques in the study of the morphology of block copolymers can be supplemented by the stress-strain and the stress-optical studies. These techniques prove to be a valuable guide in the study of morphology of copolymers when electron-microscopic studies are not possible.

The authors acknowledge financial assistance from the Defence Research Board of Canada and the National Research Council of Canada. The photographic facilities of the Department of Metallurgy and Materials Science and the DSC facilities of the Department of Chemistry were made available for this work.

This paper was taken from the Doctoral thesis of N. A. Memon submitted to the University of Toronto, 1972.

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Received September 12, 1972