

The Preparation and Physical Properties of Polyester-Poly(methyl Methacrylates) Triblock Copolymers

J. H. GREZLAK, *Department of Chemistry*, and G. L. WILKES,
Department of Chemical Engineering, Princeton University,
Princeton, New Jersey 08540

Synopsis

Block copolymers having the basic structure of PMMA-PE-PMMA were prepared by the reaction of diisocyanate-terminated polyesters with hydroxyl-terminated poly(methyl methacrylate). The molecular weights of these copolymers varied from 7,500 to 47,000. The formation of block copolymers by this method was confirmed by infrared and molecular weight analyses as well as by the physical behavior of these materials. Block copolymers of molecular weight less than 21,000 were extremely brittle in nature. The stronger copolymers of molecular weight greater than 29,000 were examined as to their dynamic modulus and stress-strain behavior. This included the effect of added homopolymer on the stress-strain behavior of such materials. To better understand their physical properties, the micelle theory of Inoue et al. was applied to these copolymers to help elucidate their morphologies.

INTRODUCTION

Since the development in 1965 of thermoplastic elastomers in the form of SBS block copolymers, block copolymers have enjoyed considerable popularity in the industrial and academic world.¹ Because of their unique physical properties and commercial possibilities, they have been the subject of numerous investigations related to their synthesis and physical properties. One system extensively studied in the laboratory of the late A. V. Tobolsky was block copolymers prepared by the polymerization of vinyl monomers initiated by macromolecular peroxy-carbamates.

This method originated in 1964 through the work of Tobolsky and Rembaum.² Prepolymers of castor oil (three hydroxyl groups per molecule), poly(ethylene-propylene adipate), or poly(propylene oxides) (one or two hydroxyl groups per molecule) were first converted to their respective isocyanate counterparts by reaction with an excess of 2,4-tolylene diisocyanate. These prepolymers were then used to prepare peroxy-carbamate-terminated prepolymers by the reaction with *t*-butyl hydroperoxide. The macromolecular peroxy-carbamate was then used to initiate vinyl polymerization of styrene, methyl methacrylate, butyl acrylate, acrylonitrile, and isoprene.

Since the initial paper in 1964, numerous studies have been performed in these laboratories to investigate and expand this basic system. These include studies

concerned with the chemistry of low molecular weight as well as macromolecular peroxy-carbamates and their role in initiating vinyl polymerization,^{3,4} new initiating systems,^{5,6} attempts to increase block copolymer formation,⁷ and the effect of reaction conditions on physical properties.⁵

This basic system offers distinct advantages over the preparation of block copolymers by anionic polymerization. It does not require the high purity associated with anionic methods. It expands the range of block copolymers preparable to the inclusion of condensation polymers. Lastly, it enables one to prepare a large variety of block copolymers through the use of one initiator and a variety of vinyl monomers and reaction conditions.

The main deficiency of this system is that it produces a material consisting of a complex mixture of graft copolymer, ABA and AB block copolymers, and A and B homopolymers, depending upon the reaction conditions employed. Structure-property relationships can therefore only be studied in a somewhat superficial manner. In view of the versatility and commercial possibilities of this system, it was therefore concluded that a model system of known composition was needed to investigate these structure-property relationships in greater detail.

Block copolymers possessing the basic structure PMMA-PE-PMMA were chosen for this study. Such a system had been previously found to yield clear, highly impact resistant plastic sheets when prepared by the Tobolsky-Rembaum method.⁸ In this work, the facile syntheses of these materials and their physical properties are described.

EXPERIMENTAL

Materials

Poly(ethylene-propylene Adipate) 80:20. Table I illustrates the samples of dihydroxyl-terminated poly(ethylene-propylene adipate) that were obtained from the Thiokol Corporation in experimental quantities. These materials were dried by heating at 70°C under full vacuum for 5 hr and used immediately.

Bis(4,4'-isocyanatocyclohexyl)methane (Hylene W). Hylene W was obtained from E. I. du Pont Co. Since isocyanate analysis indicated a purity better than 99.8%, the material was used without further purification.

Methyl Methacrylate. MMA was obtained from Borden Chemicals. It was freed from inhibitor by washing with 10% NaOH, followed by distilled water. It was dried over CaCl₂ and distilled from CaH₂ under reduced pressure and a nitrogen purge prior to immediate use.

Dibutyltin Dilaurate (T-12). T-12 was obtained from Aldrich Chemical Co. and used without further purification.

1,4-Butanediol. Butanediol was obtained from Aldrich Chemical Co. It was dried by heating at 70°C under full vacuum for 5 hr.

TABLE I
Hydroxyl-Terminated Poly(ethylene-propylene Adipate), 80:20, Obtained from Thiokol Corp.

Sample	OH number	Acid number	% H ₂ O	<i>M_n</i>
1	42.56	1.38	0.04	2600
2	60.57	1.10	0.03	1850
3	117.14	0.57	0.04	960

2-Mercaptoethanol. Mercaptoethanol was obtained from Aldrich Chemical Co. in 98% purity and used without further purification.

Benzene, Toluene, and Acetone. All solvents were of spectroquality grade. These were obtained from Matheson, Coleman and Bell and dried over Lynde 5A molecular sieves prior to use.

Petroleum Ether 30°–60°. Pet ether was obtained from Fisher Scientific Company and dried over Lynde 5A molecular sieves prior to use.

Azobisisobutyronitrile. AIBN was obtained from Borden Chemical Company and used as received.

Preparation of Homopolymer Precursors

Hydroxyl-Terminated PMMA. HO-PMMA of varying molecular weights were prepared by the polymerization of MMA in the presence of mercaptoethanol. A representative preparation and characterization is that of HO-PMMA of $M_n = 4270$. A solution of 0.0275 g AIBN, 143.5 g MMA, and 4.16 ml mercaptoethanol was prepared, degassed with CO_2 , sealed, and heated at 60°C for 28 hr. The solution was then diluted to twice its volume with acetone, hydroquinone was added, and the solvent and excess liquid reactants evaporated on a rotary evaporator. The solid was then dissolved in acetone, precipitated in water, filtered, and washed with water. This procedure was repeated three times and the polymer dried by heating at 40°C under full vacuum for seven days. The \bar{M}_n , as with all polymers possessing a molecular weight less than 15,000, was determined by vapor pressure osmometry using a Mechrolab 301A vapor pressure osmometer. The solvent employed for these determinations was benzene at 35°C. The linearity of the low molecular PMMA materials suggested the absence of significant association through hydrogen bonding. In this case, the \bar{M}_n found was 4270. The hydroxyl number was determined according to the procedure of David and Staley⁹ and found to be 14.77. This gives a value of 1.12 hydroxyl groups per polymer molecule. Table II lists the polymers prepared by this method.

Diisocyanate-Terminated Polyesters. (1) Diisocyanate-terminated polyesters were prepared in two ways. In the first method, OCN-PE-NCO of various molecular weights were synthesized by the reaction of excess Hylene W with the samples of dihydroxyl-terminated polyesters listed in Table I. A representative preparation is that of PE-1. A solution of 296.4 g polyester (hydroxyl number 42.57), 200 ml toluene and 123 g Hylene W was prepared and heated at 80°C under a nitrogen atmosphere for 72 hr. The solution was then diluted to twice its volume with benzene and precipitated in a sevenfold excess of

TABLE II
HO-PMMA Homopolymers Prepared with the Use of Mercaptoethanol as
Chain Transfer Agent

Polymer	% Mercaptoethanol by weight	M_n (VPO)	OH number	OH/molecule
PMMA-1	5.66	2770	22.4	1.11
PMMA-2	4.50	3580	17.36	1.11
PMMA-3	3.25	4270	14.77	1.12
PMMA-4	2.00	8580	7.62	1.17
PMMA-5	1.25	12900	4.77	1.11

TABLE III
Diisocyanate-Terminated Polyesters

Polymer	Precursor		ml Butanediol g PE-1	M_n
	Polymer	M_n		
PE-1	1	2630	—	3860
PE-2	2	1850	—	3560
PE-3	3	960	—	1910
PE-4	PE-1	3860	0.0145	12400
PE-5	PE-1	3860	0.0176	14700

pet ether. The solution was allowed to stand 20 hr at room temperature. The polymer was then washed several times with pet ether. It was redissolved in pet ether and the procedure was repeated two more times. The resulting polymer was then heated at 30°C under full vacuum for a period of 96 hr to give a white, sticky wax. The molecular weight by VPO was found to be 3590. Isocyanate analysis by the method of David and Staley¹⁰ indicated a functionality of 2.15 isocyanate groups per polymer molecule. Samples PE-1, PE-2, and PE-3 as listed in Table III were prepared in this manner.

(2) The second method of OCN-PE-NCO preparation called for the reaction of a diisocyanate-terminated polyester with a known quantity of butanediol. The reaction conditions employed were identical with those of the previous preparations. PE-4 and PE-5 were isolated and characterized again in accordance with the previous method and are listed in Table III. A third material having an estimated molecular weight of 30,000 was prepared similarly but used immediately in the in-situ preparation of block copolymer 3E, PMMA-PE-PMMA = 8,580-30,000-8,580.

Preparation of Polyester-Poly(methyl Methacrylate) Block Copolymers

Block copolymers having the structure PMMA-PE-PMMA were prepared by the coupling of the functional homopolymers through formation of the urethane linkage. The reactions were performed by dissolving stoichiometric quantities of the homopolymers up to 10% by weight in dry benzene, adding a few drops T-12 to catalyze the reaction and heating the solution at 65°C for a period of 200 hr. The reaction was followed to completion by monitoring infrared absorption bands. As the reaction proceeded, the hydroxyl and isocyanate absorptions at 3540 cm^{-1} and 2275 cm^{-1} , respectively, decreased while the urethane absorption at 3440 cm^{-1} increased. The polymers were isolated by precipitation from pet ether. They were purified by repeated dissolution in acetone, precipitation from pet ether, and washing with pet ether. The materials were then dried to constant weight by heating at 30°C under full vacuum. Table IV describes the block copolymers prepared in this manner.

Physical Properties

Films of all block copolymers as well as their homopolymer blended analogs were prepared by dissolving the polymeric materials to 5-10% in acetone, followed by film casting on a mercury surface. Series 3 block copolymers, i.e., those materials possessing molecular weights >29,000, were strong enough to be cast from Teflon-coated pans. Once the films were isolated, they were air

TABLE IV
Block Copolymers Prepared from the Reaction of OCN-PE-NCO with HO-PMMA

Sample	Molecular weight			PE/PMMA	Total molecular weight	
	PMMA	PE	PMMA		Theoretical	Experimental ^a
1A	2770	3860	2770	41.1/58.9	9,400	9,580
1B	2770	3560	2770	39.1/60.9	9,100	9,210
1C	2770	1910	2770	25.6/74.4	7,450	7,820
2A	4270	3860	4270	31.1/68.9	12,400	12,700
2B	4270	3560	4270	29.4/70.6	12,100	12,400
2C	4270	1910	4270	18.3/81.7	10,450	10,600
2D	8580	3860	8580	18.4/81.6	21,020	—
2E	8580	3560	8580	17.2/82.8	20,700	—
2F	8580	1910	8580	10.0/90.0	19,070	—
3A	8580	12400	8580	41.9/58.1	29,460	—
3B	12900	12400	12900	32.5/67.5	38,200	—
3C	8580	14700	8580	46.1/53.9	31,860	—
3D	12900	14700	12900	36.3/63.7	40,500	—
3E	8580	30000	8580	63.6/36.4	47,160	—

^a Molecular weight determined by vapor pressure osmometry.

dried for three days and then placed under full vacuum at room temperature for three more days.

The stress-strain properties of these materials were measured on a Tensilon Model UTM-II, Toyo Measuring Instruments Co., Ltd. Samples were die-cut in the traditional dogbone shape. The average dimensions of the samples between the clamps were 1 cm × 0.27 cm × 0.018 cm. A cross-head speed of 8 mm/min was employed. Dynamic modulus-temperature curves were obtained with a Rheovibron Model DDV-II manufactured by the aforementioned company. Sample dimensions were 3 cm × 0.32 cm × 0.018 cm, and a frequency of 11 cps was utilized.

RESULTS AND DISCUSSION

Synthesis of Block Copolymers

The basic approach to the syntheses of PMMA-PE-PMMA block copolymers was homopolymer coupling through the use of suitable functionalities as expressed in eq. (1):



Such a material is entirely free of graft copolymer and, depending on the stoichiometry and purity, should contain relatively little AB block copolymer and homopolymer impurities.

The coupling reaction chosen for this work was urethane formation through the reaction of an isocyanate with an alcohol. This reaction is known to be extremely rapid and efficient, proceeding to high conversions with few side reactions. The basic attack was therefore to prepare diisocyanate-terminated polyesters and hydroxyl-terminated PMMA and to react these materials together to yield the desired block copolymers.

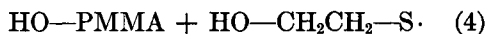
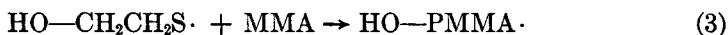
The preparation of diisocyanate-terminated polyesters proceeded easily and smoothly. As shown in Table III, polyesters of isocyanate functionalities close to

two can be readily prepared by the reaction of excess diisocyanate with dihydroxyl-terminated polyesters. As also shown, slight chain extension occurs with this reaction which could not be eliminated even with a fivefold excess of diisocyanate in dilute toluene solution. This same result had been observed earlier in preparations of polyether urethanes.⁴

The high reaction temperature and long reaction times utilized for the preparation of these materials were necessary for the prevention of unwanted side reactions. At low temperatures with catalyst, the urethane reaction is extremely fast and difficult to monitor. Furthermore, allophanate formation leading to crosslinking now becomes a competitive process which continues even at room temperature. Use of the aforementioned conditions lead to a product which is stable over a period of months.

Hydroxyl-terminated PMMA was prepared by the polymerization of MMA in the presence of mercaptoethanol as a chain transfer agent (Scheme I):

Scheme I



With relatively large amounts of mercaptan, steps (3) and (4) predominate, giving a material possessing a hydroxyl functionality close to one, as Table II illustrates. The slope of a plot of dS/dM versus $[S]_0/[M]_0$, where dS/dM is the ratio of mercaptan to monomer incorporated in the polymer and $[S]_0/[M]_0$ is the initial mercaptan to monomer charge, gives a chain transfer constant of 0.52. This compares with the literature value of 0.62 as determined by O'Brien et al.¹¹ Using 1.25% to 5.7% mercaptan, this chain transfer agent gives rise to hydroxyl-terminated PMMA in the molecular weight range of 2,770 to 12,900.

ABA block copolymers of PMMA and polyester were then prepared by the coupling of the aforementioned functional homopolymers. The reaction was followed by infrared spectroscopy which indicated block copolymer formation by the gradual disappearance of the hydroxyl and isocyanate absorptions at 3540 cm^{-1} and 2275 cm^{-1} , respectively, concurrent with the appearance of the absorption at 3440 cm^{-1} indicative of the urethane hydrogen.

Molecular weight analysis also provided evidence for this block copolymer formation. This evidence is shown in Table IV. Where molecular weight data were obtainable, the resulting materials exhibit molecular weights comparable to those predicted for block copolymer formation.

The physical behavior of these materials and their homopolymer blended analogs gave more support to the existence of block copolymers. Whereas the blended materials were brittle and translucent to opaque, the block copolymers were stronger and optically clear. This was most profoundly demonstrated with series 3 block copolymers and their homopolymer blended analogs. Whereas the series 3 copolymers were strong enough to be cast on Teflon-coated pans, the

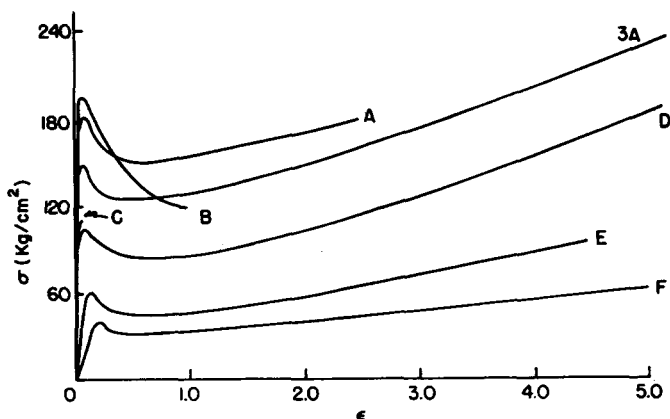


Fig. 1. Stress vs. strain of 3A block copolymer: The effect of added homopolymer: (A) 5.9% PMMA; (B) 10.5% PMMA; (C) 15.3% PMMA; (D) 6.4% PE; (E) 14.3% PE; (F) 28.5% PE.

homopolymer blends were so weak as to require a mercury surface for easy isolation.

As will be elucidated later, mechanical properties measurements also provided indirect evidence for block copolymer formation. Consider the effect of homopolymer on the ultimate tensile strength of block copolymer 3A as shown in Figure 1. As observed, a maximum exists in the curve at 0% added homopolymer, indicating both homopolymer impurities weaken the material. If this material were merely a blend of homopolymers where the tensile strength was dependent on the concentration of one or the other homopolymers, a linear behavior might have been expected over this concentration range.

Physical Properties

The most pronounced differences among these materials can be attributed to definite block copolymer and molecular weight effects. The former effect manifests itself in increased strength and improved clarity of the block copolymers when compared to their homopolymer blended analogs. The difference in clarity is readily attributed to smaller domains in the block copolymers brought about by the decreased ability of unlike polymers to separate due to the presence of covalent bonding. The difference in strength is in a large part due to the difference in molecular weight between the block copolymer and its respective homopolymer blend. For example, a homopolymer blend of PMMA of molecular weight 3000 and a polyester having a molecular weight of 3000 would have an overall molecular weight of 3000. The molecular weight of the triblock copolymer analog would be 9000. It is well known that at low molecular weights, the physical properties of polymers increase quite rapidly with molecular weight.¹²

The molecular weight factor is also quite apparent in the block copolymers themselves. Of the copolymers synthesized, only series 3 block copolymers exhibited any amount of tenacity, series one and two copolymers being extremely brittle in nature. It is therefore apparent that somewhere between the molecular weights of 21,000 and 29,000, chain entanglements become important in determining the strength of these materials.

Dynamic Modulus Behavior

Because of the strength of series 3 copolymers, these materials were further examined as to their dynamic modulus and stress-strain properties. Figures 2-6 illustrate the results obtained in the former investigation.

As shown in Figure 2, pure PMMA exhibits two transitions in its dynamic modulus behavior. The α -transition at 84°C and the β -transition at 22°C can be attributed to chain backbone motion at its T_g and rotation of the ester side chains, respectively.¹³ As is obvious from Figures 3 to 6, both of these transitions are present in the dynamic modulus spectra of PMMA-PE-PMMA block copolymers. A third transition, labeled γ , also appears in these spectra at approximately -10°C. It can be associated with the T_g of the polyester.⁷

Figures 3 and 4 show the difference between copolymers of differing A-block molecular weight. Here, two effects are observed. First of all, the α -transition appears to shift to a lower temperature as the molecular weight of the PMMA block decreases. It is attractive to attribute this shift to either (1) the expected decrease in PMMA T_g with decreasing PMMA molecular weight or (2) increasing compatibility with decreasing PMMA molecular weight. An increase in compatibility can also reduce or at least broaden the observed T_g . However, this effect may merely be due to the overlapping of the transitions involved.

The second effect is the general observation that the storage modulus at constant temperature appears to decrease with increasing soft-phase content at temperatures higher than -10°. (There also appears to be a difference in $\log E'_T$ below -10°C. This may be due to an experimental error in determining the sample dimensions. Nevertheless, when the values of $\log E'$ are shifted to identical values below -10°C, the observed differences above -10°C remain.) This is consistent with the theory of Mackensie.¹⁴ That is, above the T_g of the polyester, the polyester acts like a soft filler in reducing the overall modulus of the system.

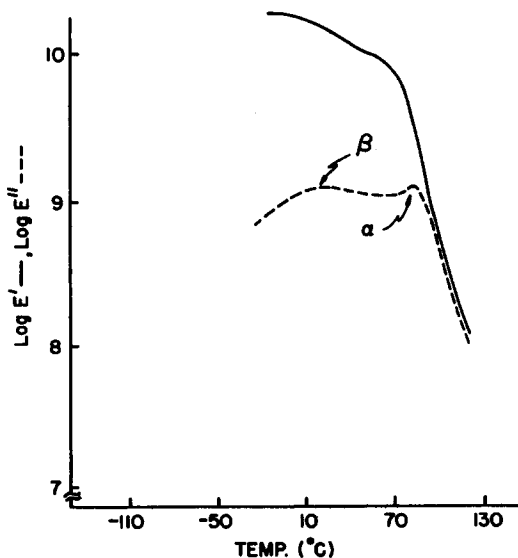


Fig. 2. $\log E'$, $\log E''$ vs. temperature for high molecular weight PMMA at 11 cps.

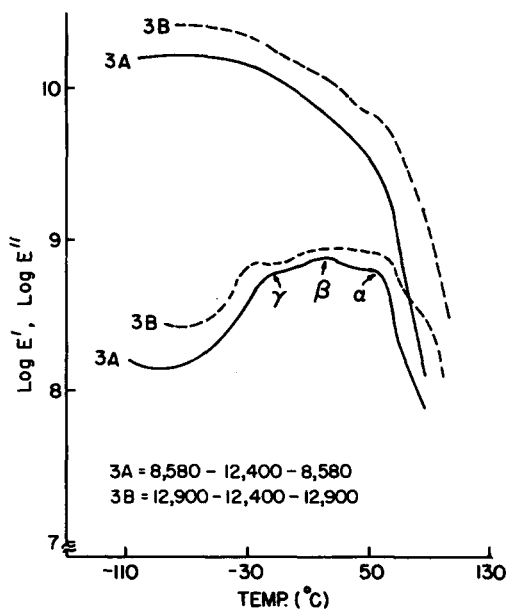


Fig. 3. $\log E'$, $\log E''$ vs. temperature for 3A = PMMA-PE-PMMA = 8580-12,400-8580 (solid line) and 3B = PMMA-PE-PMMA = 12,900-12,400-12,900 (dashed line) at 11 cps.

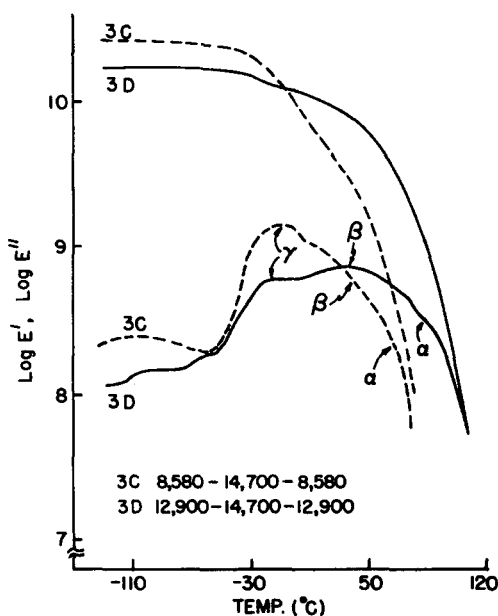


Fig. 4. $\log E'$, $\log E''$ vs. temperature for 3C = PMMA-PE-PMMA = 8,580 14,700-8,580 (dashed line) and 3D = PMMA-PE-PMMA = 12,900-14,700-12,900 (solid line) at 11 cps.

Figures 5 and 6 show the effect of polyester molecular weight on the dynamic modulus spectrum. As is most obvious from Figure 5, there is a pronounced effect of composition on the loss modulus. Because of the close proximity of the α -, β -, and γ -transitions, a broad peak is observed instead of several separated peaks. The shape of this curve is related to the overall composition of the block

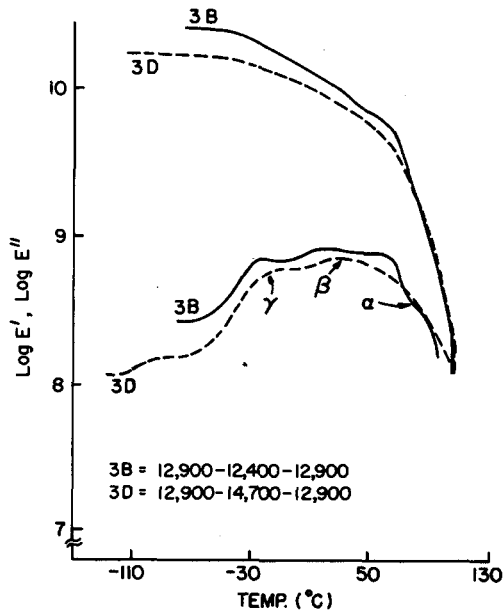


Fig. 5. $\log E'$, $\log E''$ vs. temperature for 3B = PMMA-PE-PMMA = 12,900-12,400-12,900 (solid line) and 3D = PMMA-PE-PMMA = 12,900-14,700-12,900 (dashed line) at 11 cps.

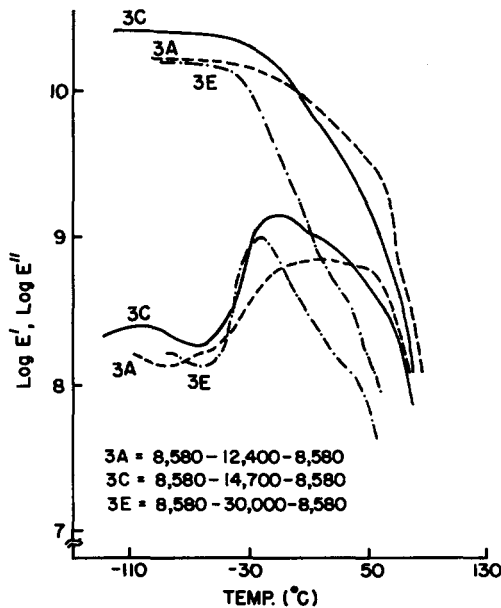


Fig. 6. $\log E'$, $\log E''$ vs. temperature for 3C = PMMA-PE-PMMA = 8,580-14,700-8,580 (solid line), 3A = PMMA-PE-PMMA = 8580-12,400-8580 (dashed line) and 3E = PMMA-PE-PMMA = 8580-30,000-8580 (dashed and dotted line).

copolymer. For example, 3A (PE/PMMA = 41.9/58.1) exhibits a fairly symmetrical peak. As the polyester content increases, this peak is skewed toward lower temperatures. At the highest percentage of polyester examined in this work (5B), this skew is pronounced to the point where the γ -transition predominates.

Stress-Strain Behavior

Table V and Figure 7 illustrate the overall stress-strain behavior of the series 3 block copolymers. As is immediately obvious, composition plays an extremely important role in determining the physical properties of these block copolymers. For copolymers 3A to 3D, as the per cent of soft phase increases, the copolymer goes from a fairly rigid material to a leathery-rubbery material. That is, the Hookian modulus and the modulus at constant elongation decrease whereas the ultimate elongation and tensile strength increase with increasing soft phase. Some of these trends are represented in Figure 8.

At first glance, these trends appear to be contradictory with the results reported for SBS rubbers. Here, σ_B decreases, ϵ_B increases, and E decreases with increasing Bd content.¹⁵ For SIS rubbers, the trends appear the same except for an independence of σ_B with composition which has been attributed to phase blending.¹⁵ However, the main difference between copolymers 3A to 3D and the SBS and SIS materials is a compositional and morphological one, and the behavior in σ_B is not really anomalous.

Consider Figure 9, which is a plot of the Hookian modulus E , σ_B , and ϵ_B for SBS block copolymers over the complete range of composition.¹⁶ Below 13% pSt, the materials are too fluid for their tensile properties to be determined. Above this concentration, E increases and ϵ_B decreases with increasing hard-phase content, consistent with a filler effect; σ_B , however, exhibits sinusoidal behavior with composition. At low per cent hard phase, where the morphology is one of styrene spheres or cylinders embedded in a pBd matrix, the pSt acts like pseudo-crosslinks, and rubbery behavior is observed. In this range, as the per cent hard phase increases, the ultimate tensile strength increases. Apparently, the pSt

TABLE V
Stress-Strain Data for Series 3 Block Copolymers*

Property	3A	3B	3C	3D	3E
E , kg/cm ²	4322	8328	1590	5076	—
σ_y , kg/cm ²	148.7	293.2	68.4	225	—
ϵ_y	0.061	0.054	0.115	0.063	—
σ_B , kg/cm ²	237.6	198.3	263.1	203.5	88.6
ϵ_B	5.17	0.269	6.0	0.80	9.66

* Strain rate = 8.0 mm/min.

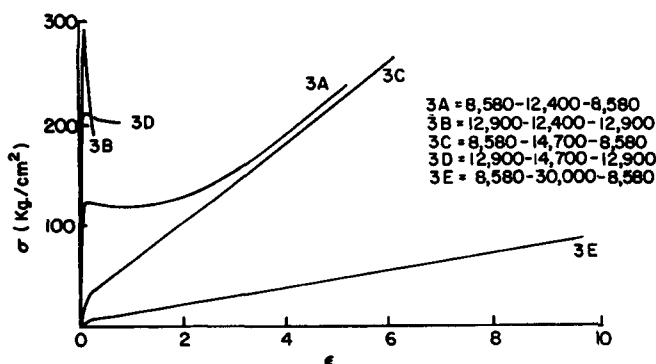


Fig. 7. Stress vs. strain curves for series 3 block copolymers.

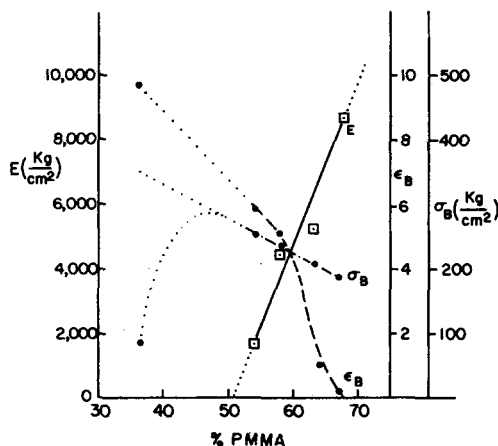


Fig. 8. Stress-strain parameters vs. % PMMA content for seires 3 block copolymers: E , ϵ_B , and σ_B represented by solid, dashed, and heavy dotted-dashed lines, respectively. Dotted lines represent extrapolations from lines determined by block copolymers 3A to 3D. Open circles represent actual values obtained for block copolymer 3E.

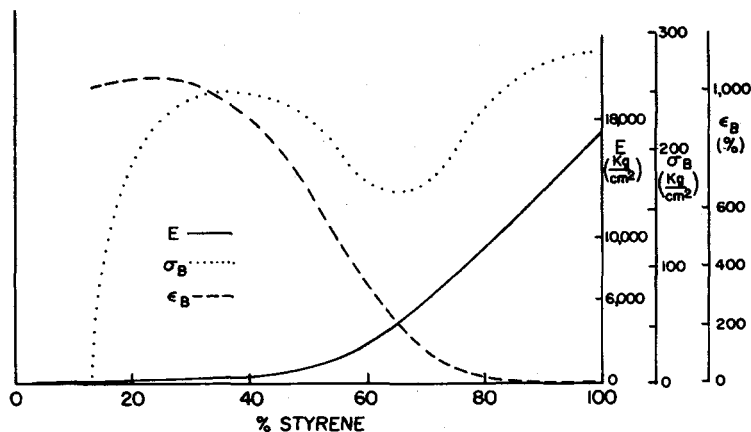


Fig. 9. Stress-strain parameters vs. % styrene content of SBS block copolymers. E , ϵ_B , and σ_B are represented by solid, dashed, and dotted lines, respectively.

behaves like firmly bound filler particles which redistribute the stress and thus prevents catastrophic rupture.¹⁷

At high percentages of pSt (60% to 100%), σ_B increases with increasing hard-phase content. Here, cylinders of the soft phase permeate the hard phase and weaken the structure. Between these two ranges at 40% to 60% hard phase lies a morphologic transition range where the structure is probably lamellar in form. It is in this range where the σ_B decreases with increasing hard phase and where 3A to 3D block copolymers appear to fall, as Figure 8 illustrates.

Figure 8 was utilized to predict the behavior of copolymer 3E (PE/PMMA = 63.6/36.4), a material which should exhibit the morphology and elastomeric behavior of SBS rubbers. Assuming near-linear behavior of E and ϵ_B with % PMMA, values of 9.64 and approximately 0 kg/cm² for ϵ_B and E , respectively, were predicted. Values of 9.66 and 0 kg/cm² were actually obtained, showing excellent agreement.

With σ_B , however, no definite quantitative prediction could be made. Assuming linear behavior of σ_B with composition, σ_B should have been 352 kg/cm². However, if these block copolymers behave similarly to the SBS materials, this value would actually be an upper limit with a true maximum existing somewhere between 36.4% and 53.9% PMMA. In accordance with these considerations, a value of 88.6 kg³/cm² for σ_B was actually observed.

This material did exhibit elastomeric behavior which was not investigated to any further extent. It exhibited a larger amount of permanent set than that associated with SBS elastomers. This may or may not be due to AB block copolymer which may have been created in the in-situ preparation of this material.

Effect of Repeated Stress and Annealing on Series 3 Block Copolymers

It has been shown that block copolymers of SBS and SIS rubbers where the % pSt is greater than 30% generally exhibit a yield point similar to that of glassy thermoplastics.¹⁵ (The magnitude of the yield stress and its discreteness may be dependent on the method of film preparation—particularly if cast from a solvent.) After one stress-strain cycle, this yield point disappears but quickly reappears upon annealing. Optical studies have given a morphologic interpretation of this behavior in copolymers consisting of pSt domains embedded in a pBd matrix.¹⁸ Here, small channels of pSt connect these domains. After one stress-strain cycle, these channels disappear but reform upon annealing. Thus, it appears that the yield point is associated with the yielding of these channels which initially form a rigid pSt network.

As shown in Figure 10, this behavior has been observed in series 3 copolymers. However, a difference in the flow properties is evident. SBS rubbers of 30%

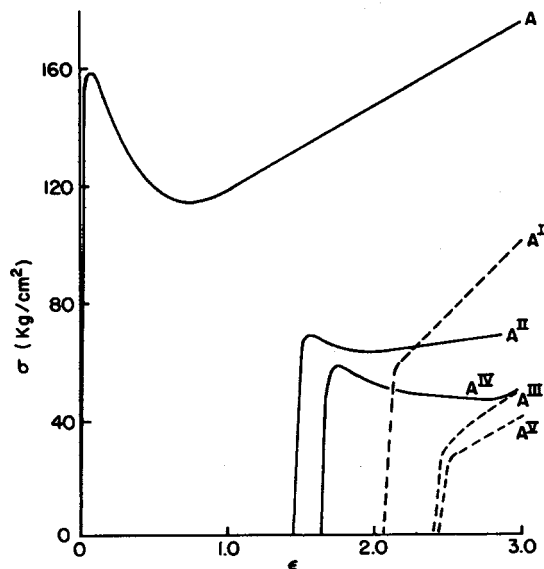


Fig. 10. Effect of repeated stress and annealing on stress vs. strain cycle of 3A block copolymer: (A) first cycle of 3A cast from acetone; (A^I) second cycle of 3A after 10 min of relaxation at room temperature; (A^{II}) third cycle of 3A after 3 hr at 55°C; (A^{III}) fourth cycle of 3A after 10 min of relaxation at room temperature; (A^{IV}) fifth cycle of 3A after 15 hr at 55°C; (A^V) sixth cycle of 3A after 10 min of relaxation at room temperature.

polystyrene exhibit a 20% set after one stress-strain cycle to 400% elongation.¹⁹ Block copolymer 3A exhibits a 66% set under similar conditions. Upon annealing, SBS rubbers recover their original dimensions, whereas a permanent set of 33% is found with block copolymer 3A. This is again most probably due to the expected lamellar morphology of this latter material. In the SBS case, most of the strain can be attributed to the uncoiling of the polybutadiene segments which recoil when the stress is removed. The temporary set is associated with deformation of the polystyrene domains which assume their original shape upon annealing. With copolymer 3A, however, two additional mechanisms may be occurring. The first is flow of PMMA segments from one lamella to another. This flow is not reversible and causes a permanent set in the material. The second is the fact that the overall molecular weight is not excessive so that some irreversible flow may be occurring.

Effect of Added Homopolymers

It has been shown for SIS copolymers (13,700–109,400–13,700) that the presence of pSt homopolymer of equivalent molecular weight as the polystyrene block increases the tensile modulus at constant elongation and has a negligible effect on σ_B until 20% homopolymer has been added.²⁰ With isoprene homopolymer of molecular weight 84,000, a level of 5% is enough to reduce this modulus by 20% and also reduce the value of σ_B as would any diluent.²⁰ This behavior and the clarity of the samples indicate that the homopolymers are incorporated into their respective block copolymer domains and is consistent with a morphology of pSt domains embedded in a pBd matrix.

Table VI and Figure 1 illustrate the stress-strain behavior of sample 3A when purposely contaminated by homopolymer. As shown, the modulus at constant elongation increases with added PMMA and decreases with added polyester. The initial Hookian modulus also tends to follow this behavior. The main difference is that the σ_B is at a maximum at 0% added homopolymer with 3A and decreases rapidly with added homopolymer, regardless of which one is added.

These results and the clarity of the samples would seem to indicate that the homopolymers are incorporated into their respective domains. This homopolymer then disrupts and dilutes the chain entanglements present in the block copolymer. Failure then occurs in a large part through the rupture of dipole-dipole interactions which is the major contribution to strength of the homopolymer. This behavior is of course most consistent with a lamellar-type morphology.

TABLE VI
Homopolymer Effect on Stress-Strain Behavior of 3A Block Copolymer

Sample	% Homopolymer	E , kg/cm ²	σ_B , kg/cm ²	ϵ_B
A	15.3 PMMA	4585	103.5	0.033
B	10.5 PMMA	3901	117.4	0.97
C	5.9 PMMA	4892	179.9	2.48
3A	0.0	4322	237.6	5.17
D	6.4 PE	3194	187.3	5.14
E	14.3 PE	1635	97.1	4.42
F	28.5 PE	936	66.4	5.01

Calculated Morphologies from the Theory of Inoue et al.

In this work, the allusion to the importance of morphology on the physical properties of block copolymers has repeatedly been made. Thus, it is of interest to know what factors determine this morphology and what the nature of the morphology is. Several studies have been performed to theoretically elucidate these details. Meier²¹ and Krause^{22,23} have treated the thermodynamics of AB block copolymers in the bulk state. Recently, Leary and Williams have expanded on such studies to include ABA block copolymers and had found that with SBS copolymers uninfluenced by solvent effects, their predictions are followed fairly well.²⁴

In the presence of solvents, the morphology has been postulated to be determined by micelle formation of the copolymer in the solvent. This micellar structure is retained in the copolymer after solvent evaporation. Optical studies by Tuzan et al.²⁵ support this hypothesis. Consequently, Inoue et al.²⁶ have presented a thermodynamic treatment of AB block copolymers based on this micelle concept, which included the molecular parameters of chain length, composition, and compatibility.

Their work²⁶ has given rise to the following expressions for the minimum free energy of formation for spherical ($G_{s,\min}$), cylindrical ($G_{r,\min}$), and lamellar ($G_{l,\min}$) structures, respectively*:

$$G_{s,\min} = (3V_A^{2/3}f_s^{-1} - (1/\gamma^2))3KTN\gamma^2 \quad (2)$$

$$G_{r,\min} = (2V_A^{1/2}f_r^{-1} - (1/\gamma^2))3KTN\gamma^2 \quad (3)$$

$$G_{l,\min} = (f_l^{-1} - (1/\gamma^2))3KTN\gamma^2. \quad (4)$$

Here,

$$f_s = \left(8V_A^{2/3} / \left[\frac{(1 - V_A^{1/3})^2}{Z_B^2 n_B a_B^2} + \frac{V_A}{Z_A^2 n_A a_A^2} \right] \right)^{1/3} \quad (5)$$

$$f_r = \left((16/3)V_A^{1/2} / \left[\frac{(1 - V_A^{1/3})^2}{Z_B^2 n_B a_B^2} + \frac{V_A}{Z_A^2 n_A a_A^2} \right] \right)^{1/3} \quad (6)$$

$$f_l = \left((8/3) / \left[\frac{(1 - V_A)^2}{Z_B^2 n_B a_B^2} + \frac{V_A^2}{Z_A^2 n_A a_A^2} \right] \right)^{1/3} \quad (7)$$

$$\gamma^3 = \Delta W / KTN \quad (8)$$

$$Z = Z_B / Z_A \quad (9)$$

where K = Boltzmann constant; T = absolute temperature; N = number of chains per unit volume; ΔW = interfacial contact energy per unit area of micelle; $Z_i^2 = \langle R_i^2 \rangle / \langle R_i^2 \rangle_0$, $\langle R_i^2 \rangle$ being the mean end-to-end distance of the i block and $\langle R_i^2 \rangle_0$ being the mean end-to-end distance of the i block theoretically represented by a chain of freely jointed segments; V_i = volume fraction occupied by the i block relative to the volume occupied by the entire block copolymer; n_i = degree of polymerization of the i block; and a_i = length of one link in the i block.

* In their original work, Inoue et al. employed the symbol σ to designate the ratio $\langle R^2 \rangle / \langle R^2 \rangle_0$. In this work we have substituted the symbol Z for σ to avoid confusion with σ_B , the ultimate tensile strength.

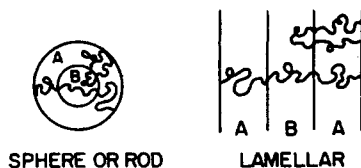


Fig. 11. Micellar structures of ABA block copolymers in solution.

If one equates

$$\psi = \left(\frac{G_{\min}}{3KTN} + 1 \right) (8/3)^{1/2} \left(\frac{[na^2]^{1/2}}{\gamma^2} \right) \quad (10)$$

where $a_A = a_B = a$ and $n_A = n_B = n$, values of $(Z_A^2)^{1/2}\psi$, a dimensionless measure of the minimum free energy of micelle formation, can be calculated for various polymeric systems and micelle configurations.

In applying these equations to the ABA system of PMMA-PE-PMMA, two approximations were made. First, the assumption was made that the ABA block copolymer could assume the general micelle configuration by bending or extension as illustrated in Figure 11. Thus, this system can be made to correspond to the equations of Inoue et al. if n_B is taken to be equal to one half the degree of polymerization of the B block. Furthermore, the second approximation is made that, since the polyester contains largely C-C linkages, $a = a_A = a_B$.

For this work, samples 3C and 3E were selected for examination. The calculated values of $(Z_A^2)^{1/2}\psi$ are shown in Tables VII and VIII. Being a measure of the minimum free energy of micelle formation, the lowest values of $(Z_A^2)^{1/2}\psi$ indicates the preferred micelle configuration of the copolymer involved (equilibrium assumed). Here, Z^3 is defined as follows:

$Z^3 > 1$, good solvent for B, poor solvent for A

$Z^3 < 1$, poor solvent for B, good solvent for A

$Z^3 = 1$, solvent of equal solvating properties

Table VII illustrates that both materials should possess a morphology where rods of PMMA are embedded in a PE matrix. Sample 3C should, however, be more lamellar in nature. This illustrates that when cast from a good solvent for the polyester but a bad solvent for PMMA, block copolymers of increasing PMMA content become more lamellar in morphology. These results were calculated for $Z^3 = 2$, which corresponds to a solvent which is a better solvent for the

TABLE VII
Values of $(Z_A^2)^{1/2}\psi$ Where $Z^3 = 2$, Calculated for Block Copolymers 3C and 3E

Structure	3C	3E
Spheres of A	0.813	0.524
Rods of A	0.715	0.501
Lamellar	0.904	0.890
Rods of B	1.413	1.222
Spheres of B	1.846	1.842

TABLE VIII
 Values of $(Z_A^2)^{1/2}\psi$ for Block Copolymer 3C Where $Z^2 = 2, 1, \text{ or } 1/2$

Structure	σ^3		
	2	1	$1/2$
Spheres of A	0.813	1.170	1.601
Rods of A	0.715	0.982	1.293
Lamellar	0.904	1.011	1.110
Rods of B	1.413	1.543	1.609
Spheres of B	1.846	2.007	2.076

polyester. This should be the case for our materials where acetone was employed as the casting solvent.

Table VIII illustrates the effect of solvent on the morphology of copolymer 3C. As shown, the preferred structure for this copolymer cast from a good solvent for the PE block is rods of PMMA. As the solvent becomes progressively better for the PMMA block and worse for the polyester, a gradual shift to the lamellar structure is favored. These results are in agreement at least qualitatively with the physical properties of PE/PMMA block copolymers reported in this work.

CONCLUSIONS

The coupling of functional homopolymers through the urethane linkage appears to be a facile way of preparing block copolymers, the only requirement being the necessary existence of active hydrogen-terminated homopolymers. Through this technique, we have prepared a variety of PMMA-PE-PMMA block copolymers of varying block chain lengths covering an overall molecular weight range of 7,500 to 50,000.

The physical properties of these materials are dependent on three main factors: overall molecular weight, the purity of the system, and its morphology, which is determined by its composition. Below a molecular weight of 21,000, all materials are extremely brittle due to the absence of chain entanglements. Above 29,000, the behavior of these materials is consistent with their expected morphologies as calculated from the theory of Inoue et al. That is, in a range of 54% to 68% PMMA where a morphology close to lamellar probably exists, the Hookian modulus increases, ϵ_B decreases, and σ_B decreases with increasing PMMA content. These materials behave more like plasticized thermoplastics rather than elastomers, possessing yield points and large amounts of permanent set upon the application of stress. Only at 36.4% PMMA, where a morphology of PMMA rods in a PE matrix is expected, is elastomeric behavior actually observed.

The purity of these materials in the range of 54% to 68% PMMA has a great effect on their physical properties; E decreases with added polyester homopolymer in accordance with a filler effect, and added PMMA has the opposite effect. Both homopolymers, however, greatly reduce the ultimate tensile strength of the overall system.

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