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Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Modification of Segmented Poly(Ether Urethanes) by Incorporation of Poly(Isobutylene)Glycol

E. Mitzner^a; H. Goering^b; R. Becker^b; J. P. Kennedy^c

^a Technische Fachhochschule Wildau WIP-Gruppen Aldershof Rudower Chaussee, Berlin, Germany ^b

Institut für Angewandte Chemie Berlin Aldersh of e.V. Rudower Chaussee, Berlin, Germany ^c Institute

of Polymer Science The University of Akron Akron, Ohio, USA

To cite this Article Mitzner, E. , Goering, H. , Becker, R. and Kennedy, J. P.(1997) 'Modification of Segmented Poly(Ether Urethanes) by Incorporation of Poly(Isobutylene)Glycol', Journal of Macromolecular Science, Part A, 34: 1, 165 – 178

To link to this Article: DOI: 10.1080/10601329708014944

URL: <http://dx.doi.org/10.1080/10601329708014944>

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MODIFICATION OF SEGMENTED POLY(ETHER URETHANES) BY INCORPORATION OF POLY(ISOBUTYLENE)GLYCOL

E. MITZNER*

Technische Fachhochschule Wildau
WIP-Gruppen Aldershof Rudower Chaussee 5
Haus 12.5, D-12484 Berlin, Germany

H. GOERING and R. BECKER

Institut für Angewandte Chemie Berlin
Aldershof e.V. Rudower Chaussee 5
Haus 4.1, D-12484, Berlin, Germany

J. P. KENNEDY

Institute of Polymer Science
The University of Akron
Akron, Ohio 44325-3909, USA

ABSTRACT

Poly(isobutylene)glycols (PIBGs) were incorporated as soft segments into poly(ether urethanes) (PEUs) prepared with poly(tetramethylene ether)glycol (PTMEG)/1,4-butanediol (BD)/4,4'-methylenebis(phenyl isocyanate) (MDI) systems. Specifically, three series of PEUs were synthesized containing mixed PIBG/PTMEG soft segments by a two-step technique in THF/DMF solvent mixtures. The polymers having different soft segment lengths, compositions, and hard segment contents were characterized by stress-strain measurements, differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and static and dynamic contact angle measurements. Substitution of even a small

amount of PIBG for PTMEG leads to a significant decrease in the tensile strength. PEUs with a mixed soft phase still have acceptable strength and elongation. However, polyurethanes containing only PIBG soft segments exhibit poor mechanical properties. According to DSC and DMA, PEUs prepared with PIBG contain a) soft domains mixed with hard segments, b) domains of well-separated hard segments, and c) hard segment domains partially mixed with soft segments. Contact angle measurements show that in the presence of ~25% PIBG the surface of the PEU is essentially saturated with the nonpolar soft segment.

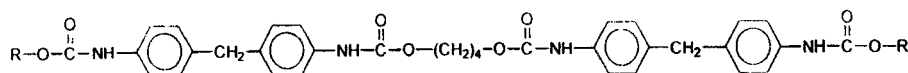
INTRODUCTION

Depending on the chemical structure and chain length of the constituents, poly(ether urethane)elastomers (PEUs) exhibit a wide variety of mechanical properties, like elasticity and strength. This structural aspect and the stoichiometry of the polyaddition, as well as the reaction conditions, influence phase separation between soft (polyether glycol) and hard (diisocyanate and diol or diamine chain extender) segments which determine the bulk properties of PEUs. The extent of phase separation in the bulk is also reflected in the surface structure [1]. Accordingly, PEU surface structures with desired properties can be tailored by the use of select monomers. The use of hydrophobic poly(dimethylsiloxane) [1-3] and polybutadiene [4, 5] as soft segments are well known.

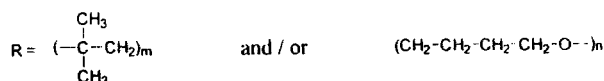
The incorporation of poly(isobutylene)glycol (PIBG) into PEUs is intriguing because of the nonpolar nature of this glycol. The presence of polar and nonpolar blocks in polyurethane chains may lead to interesting new surface structures. Investigations in the field of PIB-based polyurethanes started with networks that contained only PIBG as the soft phase [6] or PIBG/poly(tetramethylene ether)glycol (PTMEG) mixed soft phases [7]. Linear polyurethanes based on PIBG [8-10] and PEUs with soft phases containing some PIBG [1] have also been described. It has been shown [1, 7] that polyurethanes containing both PTMEG and PIBG have a single soft phase, as indicated by a single glass transition temperature (T_g), in spite of the incompatibility of the two polyols. However, PIBG-based polyurethanes have significantly less mechanical strength than conventional ones prepared with PTMEG [8-10]. Speckhard et al. [10] showed that these materials do not exhibit soft segment crystallization under strain. Another reason for the poor tensile properties of PIBG-based PEUs is their lower molecular weight relative to those of conventional polyurethanes, caused by the high degree of reactant incompatibility [10]. Polyurethanes with mixed PIBG/PTMEG soft segments chain extended with hexafluoro-1,5-pentanediol have recently been described [1]. These mixed soft segment PEUs also showed a single T_g , suggesting no phase separation within the mixed soft phase.

In the course of our fundamental studies on designed biomaterials we became interested in the possibility of assembling novel PEUs in which the conventional polar PTMEG soft segments are partially replaced by the nonpolar hydrophobic PIBG soft segments. In this manner we were willing to sacrifice mechanical properties for desirable hydrophobized surfaces. Three series of polyurethanes prepared

with mixed PIBG/PTMEG soft segments, in addition to 1,4-butanediol (BD) and 4,4'-methylenebis-(phenyl isocyanate) (MDI) are described.



MDI / BD - hard segment



PIB-chains

soft segments

PTME-chains

The soft segment chain lengths and the hard segment contents were varied. The polymers were investigated by differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), stress-strain measurements, and by contact angle measurements. A future report will concern hemocompatibility.

EXPERIMENTAL

Materials and Synthesis

Narrow molecular weight distribution tertiary chlorine telechelic polyisobutylenes were prepared by living carbocationic polymerization [11]. Quantitative regioselective dehydrochlorination by *t*-BuOK [12] followed by hydroboration/oxidation [13] led to PIBGs with primary hydroxyl endgroups (PIBG 2200: $M_n = 2200$; $M_w/M_n = 1.08$; $F_n = 2.0 \pm 0.05$. PIBG 1200: $M_n = 1200$; $M_w/M_n = 1.15$; $F_n = 2.0 \pm 0.1$).

PTMEGs Terathane 1000 and Terathane 2000 by Aldrich were used after drying in vacuum at 80°C for 2 hours. BD was obtained from Aldrich, and MDI from Pfaltz and Bauer. The PEUs (see structural formula) were synthesized in two steps as follows: NCO-terminated prepolymers were prepared by refluxing the polyol, or the polyol mixture, plus MDI in THF:DMF = 90:10 for 1.5 hours. After adding BD, this mixture was allowed to reflux for 6 hours. After this time NCO-groups were not detectable. The highly viscous PEU solution (25%) was cast in an open Teflon mold and the solvent was evaporated in a hood overnight. The PEU films were stored in a vacuum oven for 1 day at room temperature and then for 2-3 days at 50°C.

Characterization Methods

Molecular weights were determined by gel permeation chromatography in THF (concentration 0.5 wt%; injection volume 100 μl ; flow rate 1.0 mL/min) at room temperature relative to polystyrene standards. Two PLmix PS-DVB columns (10 μm) by Knauer were used with a refractive index detector. DSC thermograms

were recorded from -60 to 210°C using a Perkin-Elmer DSC 7 instrument at a heating rate of $20^{\circ}\text{C}/\text{min}$. Dynamic mechanical data were obtained using a Rheovibron DDV-IIb visco-elastometer. Data were taken from -90°C until sample failure at 3.5 Hz with a temperature rise rate of $5^{\circ}\text{C}/\text{min}$. Strips of 5 mm width and 30 mm length were used. The dielectric behavior of polyols, characterized by the complex dielectric permittivity, was measured in the -110 to 50°C range at 1 kHz by a four-probe impedance analyzer HP 4284A. The samples were filled between two gold-plated stainless steel electrodes (diameter 20 mm) with spacing of 50 ± 1 μm maintained by fused silica fibers. Room temperature stress-strain data were taken on an Instron table model tensile testing device for the samples of Series A. The crosshead speed was 5 cm/min with die-cut dog-bone-shaped test specimens (length overall 25 mm, distance between grips ~ 16 mm, width overall 6 mm, width ~ 3 mm, thickness ~ 0.3 mm). For samples of Series B, data were taken on a Tiratest 2160 instrument (Thuringer Industriewerk Rauenstein), using double the crosshead speed and larger specimens (overall length 80 mm, gauge length ~ 15 mm, overall width 15 mm, width ~ 5 mm, thickness ~ 0.3 mm). Dynamic contact angles were measured on dry samples by using a Cahn DCA-312 instrument. The test specimens were dried in vacuum for 3 days at 50°C . Both advancing and receding angles were obtained at a platform speed of 0.15 mm/sec. The averages of 10 measurements (two cycles for each of five test specimens per sample) using double-distilled water as test liquid are reported. Static contact angles were taken on a Kruss G 40 instrument equipped with a video system and automatic analysis. Five drops (0.4 μL) of double-distilled water were measured 30 times every 1.5 second on dry samples. The standard deviation of the dynamic method was $\pm 1^{\circ}$ and that of the static one $\pm 2^{\circ}$.

RESULTS AND DISCUSSION

Mechanical Properties

The composition, molecular weight characteristics, and mechanical properties of PEUs prepared in three series of experiments are presented in Table 1. The heading of the table shows the synthesis charges used in the three series in terms of PIBG + PTMEG/BD/MDI molar ratios. Columns 1–3 give our sample symbols identifying the series (A, B, or C) and the wt% PIBG used to make up the soft segment and the sum of the two components of the hard segments (BD + MDI) used for the synthesis, respectively. Columns 4–6 give molecular weight characteristics, Columns 7 and 8 show mechanical properties, Columns 9–11 give DSC melting peaks (first run), and Columns 12–14 show the results of dynamic contact angle measurements.

In regard to the mechanical properties of the PEUs of Series A, the data show a strong decrease in tensile strength and a lesser decrease in elongation with increasing PIBG content. This effect is due to the decrease of the hard segment content which in turn was caused by the fact that the molecular weight of PIBG was more than double that of the PTMEG. The dramatic decline in the mechanical properties in A-PIB100 is nonetheless remarkable and probably reflects the absence of reinforcing H-bridges in this PU.

TABLE 1. Characterization Data of PEUs:

Series A: PTMEG 1000 + PIBG 2200/BD/MDI = 1/2/3

Series B: PTMEG 2000 + PIBG 2200/BD/MDI = 1/2/3

Series C: PTMEG 1000 + PIBG 1200/BD/MDI = 1/1.5/2.5

1	2	3	4	5	6	7	8	9	10	11	12	13	14
PEU	PIBG soft segment wt%	Hard segment wt%	M_w , g/mol	M_n , g/mol	M_w/M_n	Tensile strength MPa	Elongation %	T_g , °C	T_{m2} , °C	T_{m3} , °C	Advancing angle Θ_A , degrees	Receding angle Θ_R , degrees	Hysteresis $\Theta_A - \Theta_R$, degrees
A-PIB0	0	48	69,400	18,300	3.8	36.8 ± 2.4	490 ± 10	70	154	—			
A-PIB28	28	44	61,700	18,400	3.4	28.2 ± 0.4	470 ± 10	72	155	167			
A-PIB51	51	39	52,900	16,000	3.3	18.0 ± 0.9	410 ± 25	72	154	165			
A-PIB72	72	34	55,700	16,400	3.4	16.3 ± 1.5	370 ± 35	71	152	166			
A-PIB100	100	30	23,700	9,500	2.5	6.6 ± 0.2	113 ± 7	69	160	179			
B-PIB0	0	32	50,700	18,200	2.7	23.4 ± 0.6	1260 ± 60	82	170	—	92	59	33
B-PIB5	5	32	46,500	21,300	2.2	16.3 ± 2.3	1080 ± 150	81	168	—	99	59	40
B-PIB10	10	32	53,300	13,600	3.9	14.2 ± 0.5	1210 ± 45	79	164	175	101	59	42
B-PIB15	15	32	54,900	17,400	3.2	14.1 ± 0.5	1030 ± 35	80	164	178	99	59	40
B-PIB20	20	32	36,500	14,500	2.5	13.1 ± 0.8	1070 ± 90	81	163	180	101	60	41
B-PIB25	25	32	39,800	13,000	3.1	13.2 ± 0.8	1070 ± 85	82	164	180	103	57	46
B-PIB100	100	30	17,100	7,500	2.3	4.1 ± 0.1	100 ± 5	83	162	182	106	57	49
C-PIB0	0	43	35,200	9,900	3.5			70	141	—	87	55	32
C-PIB27	27	42	28,800	8,300	3.5			65	142	171	103	50	53
C-PIB50	50	41	24,400	7,700	3.2			70	150	170	104	51	53
C-PIB73	73	40	24,600	7,100	3.5			75	155	164	105	52	53
C-PIB100	100	39	14,800	5,600	2.6			75	160	172	105	56	49

Not determined

Not determined

In Series B the molecular weights of the PIBG and PTMEG were very similar ($M_n = 2200$ and 2000 , respectively) so that the changing of the relative weight ratio of these components did not appreciably affect the overall hard segment content (i.e., the hard segment content remained constant with ~ 32 wt%). Interestingly, the replacement of only 5% PTMEG by PIBG causes a very significant drop in tensile strength (from 23.4 to 16.3 MPa). However, after this dramatic initial decrease a further enhancement in PIBG content causes a much smaller effect; indeed, the data hardly change in the PIBG = 10–25% range. A comparison of the strength values of sample A-PIB72 with those of samples from B-PIB5 to B-PIB25, in other words, samples whose hard segment contents are about the same, seems to indicate that the tensile strengths are largely independent of the molecular weight of the soft segments and depend only on the hard segment contents. In regard to elongations, the values are more or less unaffected by the PIBG content. The elongations of Series B are conspicuously higher than those of Series A. This phenomenon is due to the higher molecular weight of PTMEG used in the former series.

In sum, according to these studies, PEUs having PIBG soft segments exhibit much poorer mechanical properties than those with PTMEG soft segments [see also Refs. 8–10], most likely because of the absence of reinforcing H-bridges in the formers. The replacement of only 5% PTMEG with PIBG causes a dramatic loss in tensile strength and elongation. However, the effect is much diminished by a further increase in the PIBG content. Elongations are chiefly determined by the soft segment length. While the mechanical properties of PEUs containing PIBG are lower than those of high quality PEUs, if the PIBG content is less than ~ 15 wt%, the values are still quite acceptable for many applications, particularly for biomaterial uses. The trade-off for diminished mechanical properties is hydrophobic surfaces (see below).

Bulk-Phase Characterization by DSC and DMA

While reliable glass transition temperatures (T_g) of the rubbery phase could not be obtained by DSC on account of the relatively small amount of well-separated amorphous soft phase, this technique gave satisfactory melting points (T_m) in regard to the hard segments. Figure 1 displays the DSC traces of Series B samples, and Table 1 lists T_m data for all materials. The sharp melting endotherms in the 3–10°C range shown in Fig. 1 are due to the crystalline parts of the PTMEG of $M_n = 2000$. While these peaks are quite prominent in samples containing less than 15% PIBG, they are absent in the presence of more than 15% PIBG soft segments or in samples prepared with the lower molecular weight PTMEG ($M_n = 1000$, Series A and C). Evidently, the shorter PTMEG segments do not crystallize in our PEUs.

The broad transition regions with the relative maxima in the 65–85°C range, exemplified in Fig. 1 and collected in the T_i column of Table 1, are caused by nonequilibrium phases because they disappear upon annealing (i.e., heating above the melting range followed by quenching after the 2nd heating cycle). These phases most likely consist of mixed soft and hard segments. There is no direct correlation between this transition and the PIBG content found.

The melting of the hard phase starts above $\sim 140^\circ\text{C}$. The corresponding melting endotherms are quite broad because of the ill-defined morphology (different

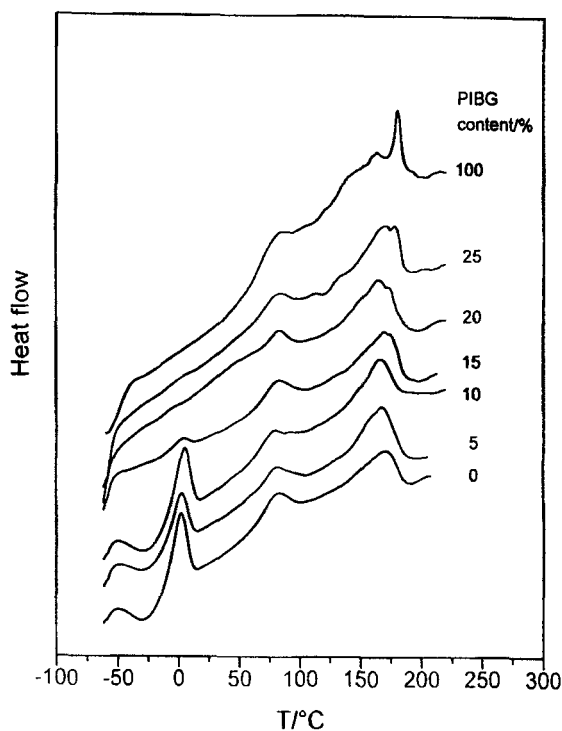


FIG. 1. DSC traces of PEUs (Series B initial run).

size domains, different interface thickness, etc.). The maxima of the endotherms, T_{m2} , are listed in Column 10 of Table 1. The PEU containing only PTMEG 2000 soft segments shows, like all pure PTMEG/PEUs, only one high temperature melting endotherm, i.e., B-PIB0 with $T_{m2} = 170^{\circ}\text{C}$. The lower molecular weight of PTMEG in Series A and C causes a decrease of T_{m2} . Interestingly, substituting 10% or more PIBG for PTMEG produces a second high temperature melting peak, T_{m3} , indicating the appearance of a new, better-defined hard phase (improved phase separation, sharper interfaces). Similarly to these observations Yoon et al. [1] also found a second high temperature melting endotherm in PEUs chain-extended with hexafluoro-1,5-pentanediol; however, the second peak appeared only in the presence of 20% PIBG. The fact that the second melting peak is about 10°C higher in PUs prepared with PIBG 2200 (i.e., in A- and B-PIB100) than those obtained with lower molecular weight PIBG 1200 (i.e., in C-PIB100), suggests that the phase separation of the well-defined hard segment domains is easier with the high molecular weight soft segments. The severe overlap of the T_{m2} and T_{m3} endotherms precluded a more detailed analysis of the hard domains of PEUs containing mixed soft segments.

Dynamic mechanical analysis (DMA) gave more detailed information as to the compatibility between PIBG and PTMEG soft segments, and between both types of soft segments and the hard segments. Figure 2 displays the storage modulus

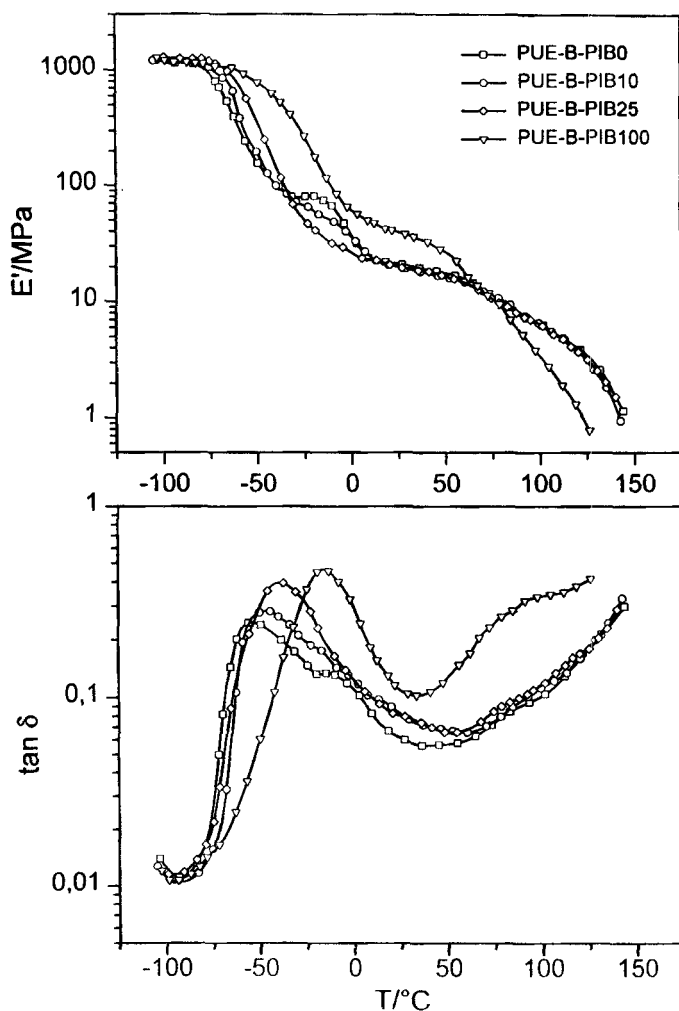


FIG. 2. Storage modulus (E') and mechanical loss factor ($\tan \delta$) of select PEUs as a function of temperature (Series B).

(E') and the mechanical loss factor ($\tan \delta$), that is, the loss modulus (E'') divided by E' , of PEUs of Series B as a function of the temperature at a fixed frequency. The relaxation spectrum of B-PIB0 shows a well-pronounced four-phase system. The T_g s of the phase-separated soft segments are indicated by the dropping of E' and the maximum of $\tan \delta$ (see Fig. 2). The T_g values given in Fig. 3 were determined from the maximum of E'' , i.e., for B-PIB0 at -64°C .

The decrease of the modulus in the -15 to 10°C range is caused by the melting of crystalline PTMEG segments. Although the PEU is linear, chain mobility (melting) cannot be observed above this temperature range, rather, the material shows rubberlike elasticity as indicated by a plateau of the modulus over a wide temperature range. This behavior is due to an aggregation of hard segments to

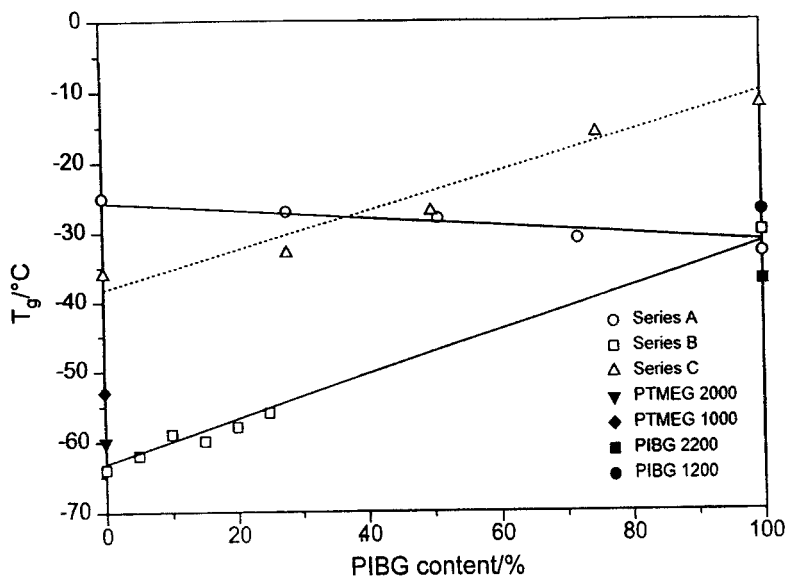


FIG. 3. Glass transition temperatures of PEUs as a function of the PIBG content [Series A, B, and C determined by DMA (E''), polyols determined by dielectrical measurements].

microdomains of significant thermal stability. The coherence of the crosslinks is most likely caused by cooperative hydrogen bridges between hard segments. Above $\sim 145^\circ\text{C}$, chain mobility sets in and the PEU loses dimensional stability ($E' < 1$ MPa). Substantial melting of the hard domains appears at an even higher temperature, as indicated by DSC (see Table 1). Prior to melting, the modulus drops slightly in the $60\text{--}90^\circ\text{C}$ range, indicating a transition due to a mixed phase of hard and soft segments. (See also the weak endotherm in the DSC scans in Fig. 1.) The position of this transition is determined by preparation conditions and is insensitive to structural variations of the PEUs.

All Series B samples show well-defined single glass transitions. With increasing PIBG content the T_g s shift to higher temperatures. As seen in Fig. 3, the magnitude of this shift is similar to the difference (23°C) between the T_g s of PTMEG 2000 and PIBG 2200; the T_g s of the latter obtained by dielectric relaxation spectroscopy are shown in Fig. 4. In contrast to Yoon et al. [1] who assumed that the T_g s of these polyols are similar, we found a significant difference in the T_g s. The T_g of the PEU made with PIBG is a little higher than expected from the T_g of the starting material, which suggests a partial mixing of soft and hard segments. The extent of this phase mixing may be larger than with PEUs prepared with PTMEG. Also, the mechanically indicated melting point (the melting point when E' is decreased to 1 MPa) of the PEU prepared with PIBG, that is, about 20°C lower than of all other samples of Series B (Fig. 2), corroborates this result, although according to DSC the highest melting point by the high temperature endotherm T_{m3} (Column 11 of Table 1) was found for this material. In agreement with DMA, the first melting peak in the high temperature region of the hard domains (T_{m2}) decreases with

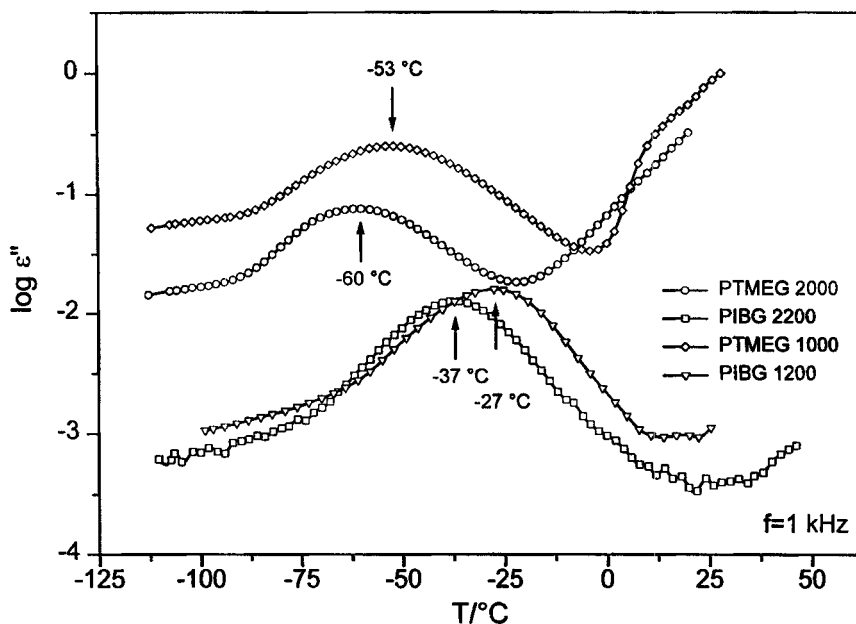


FIG. 4. Dielectric loss ϵ'' of polyols as a function of temperature.

increasing PIBG content in Series B. This result may be due to two types of hard domains: 1) highly ordered hard domains and 2) hard domains whose aggregation is disrupted by interdispersed soft segments and/or fringed phase boundaries. Partial mixing of soft and hard segments is also indicated by the strongly decreasing modulus with increasing temperature and by the absence of a rubbery plateau.

Figure 5 displays E' and $\tan \delta$ as function of temperature for select PEU samples of Series A, B, and C. In agreement with DSC results, soft segment crystallization cannot occur in PEUs prepared with PTMEG 1000. As expected, the T_g of A-PIB0 is higher by about 40°C than that of B-PIB0, i.e., the PEU containing a molar equivalent of the higher molecular weight PTMEG. As pointed out above, this is caused by the forced mixing of soft and hard segments in the case of the shorter soft segments. Evidently the T_g s reflect the existence of soft phases partially mixed with hard segments. Because the hard segment content of A-PIB0 is significantly higher than that of B-PIB0, the former shows higher modulus values above T_g but, as expected, the same melting point. The mixed soft segments of Series A show only one T_g whose decrease with increasing PIBG content (Fig. 3) is a result of the substitution of shorter soft segments (PTMEG 1000) with longer ones (PIBG 2200).

The PEUs of Series C are not directly comparable with the samples of Series A and B because not only the molecular weights of the soft segments but also the molar ratio of the components are different. The lower T_g and lower modulus values above T_g , as well as the lower melting point of C-PIB0 in reference to A-PIB0, is not surprising. As reflected in Fig. 3, increasing the PIBG content leads to increased T_g s, as shown by the samples of Series B. As in the latter case, this is due to the similar molecular weights of the two mixed soft segments but having different T_g s.

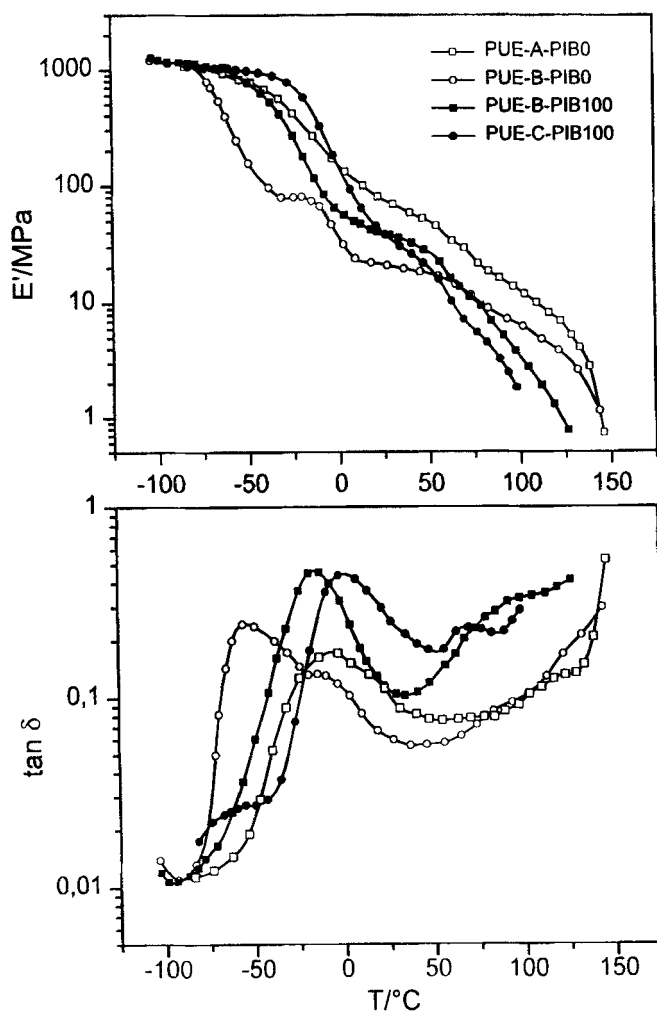


FIG. 5. Storage modulus (E') and mechanical loss factor ($\tan \delta$) of select PEUs with PTMEG or PIBG soft phase as a function of temperature (Series A, B, and C).

Evidently they pass through one glass transition process as homogeneous polymer systems. Relative to Series B, the T_g s of the PEUs of Series C are higher. Furthermore, the difference between the T_g s of PTMEG 1000 and C-PIB0 is noticeably larger than that between the T_g s of PTMEG 2000 and the corresponding B-PIB0. Both indicate a higher hard segment content in the soft phase because of the shorter soft segments in comparison to Series B. For the same reason the T_g s of C-PIB100 on the one hand and A- or B-PIB100 on the other hand are clearly different. As shown in Fig. 5, the modulus values in the plateau region of A-PIB100 and C-PIB100 are different because of the different hard segment contents. The melting points of these materials are nearly the same.

According to these data, then, both soft phases PTMEG and PIBG may to a certain extent mix in PEUs with the hard phase. Similar conclusions have also been

reached by earlier investigators [1]. Furthermore, the findings show two, at the first sight contradictory, tendencies. On the one hand, the incorporation of PIBG leads to better hard phase separation. However, on the other hand, phase mixing between hard and soft segments is also evident. It seems as though PEUs may contain side-by-side both well-separated hard phases *and* hard phases mixed to a certain extent with soft phases.

Surface Characterization by Contact Angle Studies

The surfaces of our PEUs were studied by both static (sessile drop) and dynamic (Wilhelmy balance) contact angle characterization methodologies. The results are collected in Fig. 6 and Table 1. According to the static contact angles, conventional PEUs containing only PTMEG soft segments (A- or B- or C-PIB0) exhibit relatively low contact angles, indicating relatively hydrophilic surfaces. However, as soon as even a small portion of PTMEG soft segments is replaced by PIBG (i.e., by 5% in Series B), the contact angles start to increase, suggesting a rise in the hydrophobicity. The effect is quite obvious even at 5% substitution (see Series B in Fig. 6). However, additional substitutions do not produce a linear response and the effect tends to level off at or not much beyond $\sim 25\%$ PIBG. Similar observations have also been made with Series A and C samples (see Fig. 6). Evidently, the outer surfaces become essentially covered with the hydrophobic PIBG at $\sim 25\%$ PIBG soft segments.

This phenomenon can be readily explained, for example, by Takahara et al.'s model [14]. Thus, since air is highly hydrophobic, in the dry state the hydrophobic soft segments tend to occupy the outer surfaces and tend to displace the relatively

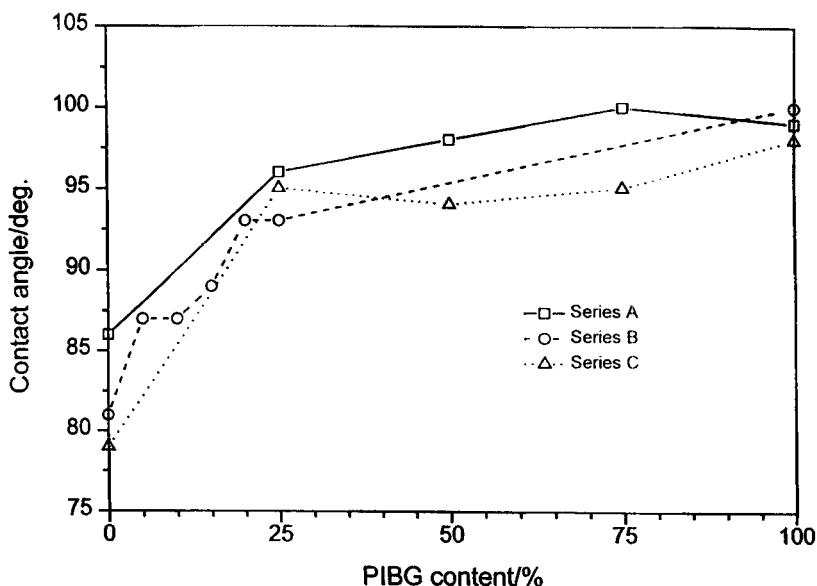


FIG. 6. Static contact angles of PEUs as a function of the PIBG content (Series A, B, and C; test fluid: water).

more polar hydrophilic PTMEG soft segments and much more polar hard segments. By increasing the relative amount of PIBG, these chains will also tend to move toward the outer hydrophobic surfaces. After the surfaces become saturated with the most hydrophobic component, further increasing the PIBG content will not further raise the contact angles (i.e., hydrophobicity will not further increase).

Dynamic contact angle studies by the use of the Wilhelmy plate balance were carried out only with Series B and C because of the almost constant hard segment content in these series (in contrast to Series A). The PIBG content was the only parameter varied. These measurements (Columns 12–14 of Table 1) corroborated and expanded the results of the static studies. According to these findings the advancing contact angles (Θ_A) of all the samples were higher than 90° , which shows that the products possessed hydrophobic surfaces when they were submerged in water. In contrast, all the receding contact angles (Θ_R) were much less than 90° , which indicates that the surfaces emerging from water were in fact hydrophilic. The contact angle hysteresis ($\Theta_A - \Theta_R$) indicates the magnitude of this effect. Evidently these processes involve a rapid hydrophobic \rightarrow hydrophilic surface rearrangement when the dry materials are submerged in water and, conversely, a rapid hydrophilic \rightarrow hydrophobic reorganization when the test specimens are withdrawn from water into air [15]. This reorganization is reversible (cycles 1 and 2 by the Wilhelmy plate balance experiments gave close to identical responses) and is sufficiently rapid (< 1 minute) to respond to the environmental changes during the time scale of the measurement.

The contact angle hysteresis is quite evident even with samples that do not contain PIBG (see B- and C-PIB0); however, it becomes more pronounced in the presence of the strongly hydrophobic PIBG. As shown by the data of Series B, the hysteresis increases noticeably, i.e., from 33 to 40, substituting 5% of PIBG, and it tends to rise, albeit slower, up until $\sim 25\%$ PIBG is introduced. Beyond this level of substitution the hysteresis does not seem to rise further (the rise from 46 for B-PIB25 to 49 for B-PIB100 is within experimental variation). The hysteresis effect may also be caused by surface roughness [16]; however, according to atomic force microscopy, the surfaces of the Series B samples were relatively smooth (micrographs not shown).

In sum, these contact angle studies suggest that the surface of PEUs containing PIBG soft segments tend to be hydrophobic. Even a small amount ($\sim 5\%$) of PIBG is sufficient to start surface hydrophobization. However, the effect reaches saturation with $\sim 25\%$ PIBG, and additional PIBG does not further augment the hydrophobicity of PEU surfaces.

CONCLUSIONS

PEUs containing both PTMEG and PIBG soft segments have been prepared, and select surface and mechanical properties investigated. According to DSC and DMA studies, our PEUs exhibit complex morphologies and contain a variety of domains, i.e., domains of soft segments mixed with hard segments, domains of well-separated hard segments, and domains of mostly hard segments containing a limited extent of soft segments. The introduction of PIBG causes strong surface hydrophobization: The effect is strongly noticeable with $\sim 5\%$ of PIBG in the soft

phase, and reaches a saturation level with ~25% PIBG. While the substitution of PIBG for PTMEG segments decreases the tensile strength and elongations, the hydrophobized PEUs still possess adequate mechanical properties for biomaterials use.

ACKNOWLEDGMENTS

E.M. is grateful to the Deutsche Forschungsgemeinschaft for fellowship support. This research was partly supported by the National Science Foundation (Grant 94-23202). The determination of polyol T_g s by Dr. A. Schoenhals and of molecular weights by Dr. G. Schulz is gratefully acknowledged.

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Received January 26, 1996

Revision received April 30, 1996