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13. ABSTRACT (Maximum 200 words)

We have studied the viscoelastic behavior of polyurethane melts to obtain a greater fundamental understanding of phase separation in multiblock polyurethane copolymers with coulombic and coordination interactions. Two series of non-crystallizable aliphatic polyurethanes and its cationmers that flow at relatively low temperatures and are more thermally stable than commercial materials were synthesized. The effects of three principal parameters (block length N, block incompatibility χ, and composition) on microstructure and rheological properties of polyurethane elastomers were examined.

A separate part of this report involves synthesis and characterization of polyurethanes with monodisperse, hydrophobic soft segments. We have prepared and evaluated the mechanical and solvent sorption properties of a series of polyurethane elastomers based on three different types of soft segments with five different molecular weights. Both mechanical and solvent sorption properties are found to be dependent on hard segment content, hard segment chemistry, properties of the polyol, and the order of the hydrogenation and polymerization reactions.

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Introduction

Polyurethane elastomers are microphase-separated multiblock copolymer of the type $(AB)_n$ where at the service temperature one block of the material is glassy or semicrystalline, and the other block is soft or rubbery. Polyurethane chemistry offers tremendous versatility, and an almost limitless variety of chemical components and compositions are possible. The resulting wide range of physical properties have led to commercial applications of polyurethanes in such areas as flexible foams, tough elastomers, engineering thermoplastics, and durable coatings. They owe their good elastomeric properties to microphase separation of the blocks driven by segmental incompatibility. Micro-phase separation can be further enhanced by interurethane hydrogen bonds and/or crystallization. Consequently, microphase separation can occur at segment molecular weights lower than 1000. This is in marked contrast to the amorphous styrene-diene block polymers where due to weaker van der Waals interactions, microphase separation requires segment molecular weights approaching 10,000. Since phase mixing is entropically favored, an increase in temperature can cause a Microphase Separation Transition (MST) from a microphase separated to a single phase state. Such a MST has been studied extensively in diblock and triblock systems by scattering, calorimetric and rheological methods. There have been a few studies of phase mixing in polyurethane elastomers and they have concentrated on Small-Angle X-ray Scattering (SAXS) and Differential Scanning Calorimetry (DSC) to distinguish a phase mixed state to a microphase separated one. Rheological studies of polyurethanes have been rare and even the effects of important variables such as block length, composition and block incompatibility have not been documented. The primary reason for this is that the urethane linkage is not thermally stable over time scales of rheological tests at the high temperatures required for the melt state of polyurethane elastomers. Our research aimed at obtaining a greater fundamental understanding of phase separation in multiblock polyurethane copolymers with coulombic and coordination interactions. Knowledge from such investigations is important in the development of new and improved materials, and in tailoring polymer properties by varying processing conditions.

Polyurethanes with hydrophobic soft segments are of interest for use in a variety of applications. The inertness of the olefinic segment coupled with the strong microphase segregation in these systems lends these materials many desirable characteristics, such as solvent resistance, good electrical properties, low moisture permeability, and biocompatibility. When the soft segments are fully saturated, the chemical inertness is improved even further, and the materials gain resistance to hydrolysis and oxidation. This chemical inertness, coupled with their inherent processability makes these olefinic urethanes attractive for use in barrier applications including protective clothing, masks and gloves. Polyurethanes based on monodisperse hydroxy terminated polybutadiene (HTPBD) soft segments are almost completely phase-separated materials due to the large polarity differences in the soft and hard segments. Branching in soft segment can completely or partially prevent crystallization, which makes these materials excellent candidates for applications where transparency is an important consideration. In a separate part of this project, we investigated a novel series of polyurethanes based on hydrogenated HTPBD soft segments and two different hard segments. These soft segments are unique in that they are produced by a cost-effective process, have functionality of nearly exactly 2.0, and have very low branch content in comparison to commercially available HTPBD polyols. Our aim was to produce melt-processable polyurethanes with elastomeric mechanical properties, transparency, and good resistance to the sorption and diffusion of solvents.

Focused Research

Our research was focused on two separated areas: studies of the rheology and microphase separation on polyurethanes and polyurethane ionomers, and studies on polyurethanes with hydrophobic soft segments as barrier materials.

The first area of investigation aimed at obtaining a greater fundamental understanding of phase separation in multiblock polyurethane copolymers with coulombic and coordination interactions. There are three principal parameters that govern the properties of polyurethane elastomers: block length N, block incompatibility χ, and composition. The effects of these parameters on microstructure and rheological properties of polyurethane elastomers were studied by synthesizing two series of materials that will flow at relatively low temperatures and be more thermally stable than commercial materials. This was done by eliminating crystallinity at high temperatures, by employing thermally stable aliphatic urethanes, and by using polyurethane cationomers as model systems to study the rheological properties of non-ionic polyurethanes.

The first series of polyurethanes that studied the effect of block length, has the structure shown in Figure 1. The soft segment is polycaprolactone diol (PCL) with various molecular weights (830, 1000, 2000, 3000) and the hard segment is composed of isophorone diisocyanate (IPDI) and 1,4-butanediol (BD). The sample designation E-xx refers to the soft segment molecular weight; all materials have a composition close to 50% soft segment by weight. The second series, also shown in Figure 1 studied the effect of block incompatibility at fixed segment length. The soft segment is polypropylene glycol (PPO) and the hard segment is composed of IPDI and dimethylamino-1,2-prooanediol. Quaternization of the chain extender with methyl iodide allows us to increase the incompatibility by making the hard segment more polar. The sample designation is I-xx-yy, where yy denotes the percentage of chain extender quaternized. Even though this series is strictly an ionomer, no evidence of ionic association of the quaternary ammonium iodide groups was found. It has been demonstrated that the reason for the higher incompatibility is stronger hydrogen bonding within the hard segment phase due to hydrogen bonds between >N-H and the iodide ions.

The degree of phase separation was defined using the glass transition temperature of the soft domains as determined from dynamic mechanical thermal analysis (DMTA) and the changes in specific heat at the glass transition, to be measured by differential scanning calorimetry (DSC). Small-angle X-ray scattering (SAXS) was used to characterize the polymer microstructure, and also provided another measurement of phase separation. Qualitative comparisons of hard domain cohesion were obtained from tensile properties and the temperature of the upper transition in DMTA.

The second area of our research involves synthesis and characterization of polyurethanes with monodisperse, hydrophobic soft segments. This is a part of an effort at the Army Research Laboratory to develop polyurethanes for protective fabric coating applications. We have prepared and evaluated the mechanical and solvent sorption properties of a series of polyurethane elastomers based on novel soft segment with five different molecular weights(provided by Prof. Ferene Tudous, Dept. of Macromolecular Chemistry, CRIC, Budapest, Hungary), as well as a series of polyurethane elastomers produced using commercial soft segments of similar chemistry. Properties are found to be dependent on hard segment content, hard segment chemistry, properties of the polyol, and the order of the hydrogenation and polymerization reactions.

Major Results

Microphase Separation and Rheology in Polyurethanes and Polyurethane Ionomers

Microphase Separation

In E-series, the polyester soft segment crystals were melted at 50°C before testing (DSC showed no crystalline melting endotherms above 50°C; nor was there recrystallization after several hours at room temperature.). Samples E-830 and E-1000 show no feature other than a single broad glass transition, while samples E-2000 and E-3000 show transitions at much lower temperatures which are characteristic of a microphase-separated polyurethane. The onset temperatures of such transition decrease with increasing block length, approaching the T_g of the pure soft segment (Table 1). This has commonly been regarded indicative of increasing phase purity. Annealing at 200 °C for 4 min. causes almost no change in the DSC curves; i.e., the phase compositions are the same at 200 °C as at 55 °C. Quantitative analysis of DSC curves indicates that the measured ΔCp's of E-830 and E-1250 are very close to those calculated ones assuming a single-phase sample. In contrast, the measured values for E-2000 and E-3000 are appreciably lower than those calculated, implying that only a part of the total soft segment contributes to the soft-segment glass transition; the rest is mixed with the hard-segment phase and plays no role in the soft-segment transition. Thus, as observed by DSC, E-830 and E-1250 are in a single-phase state, whereas E2000 and E3000 are progressively more microphase-separated.

The thermal properties of the I-series of polyurethanes, the pure PPO precursors, and the hard segment IPDI/DMP quaternized to various extents was measured directly by DSC. The hard segment (IPDI/DMP quaternized to various extents) T_g increases with the extent of quaternization and the ΔC_p at the glass transition is found to be 0.38 J/(g K) for all the quaternized hard segments.

The DSC data for the I-series and their corresponding pure soft segments are summarized in Table 2. The I-725 series show a broad glass transition at a temperature intermediate to that of the pure hard and soft segments. The I-1000 series exhibit two poorly resolved glass transitions, followed by a distinct endotherm at about 60°C. Similarly, though somewhat more intense, endotherms are found in I-2000 series. The mechanisms responsible for these endotherms are not well understood, but they are highly sensitive to thermal history. Annealing at 55°C overnight completely erases the endotherm. Qualitatively, the unquaternized materials show a decrease in T_g as block length increases indicative of better microphase separation. Within each series, the T_g does not change significantly with increasing quaternization, except in the I-1000 series where the T_g becomes better defined. This is somewhat surprising since more quaternization is expected to improve microphase separation and hence lower the T_g. However, there is a competing effect: as quaternization increases, the T_g of the pure hard segment increases as well. Since some hard segment is usually dissolved in the soft-segment-rich phase, it causes the T_g of the soft segment phase to increase. Evidently, this is enough to offset the lowering of T_g due to better microphase separation. This also implies that the I-725 series is not completely homogeneous. In summary, DSC data indicate that microphase separation increases with block length (I-725 series was almost homogeneous, whereas the I-2000 series was almost completely microphase separated) and there is no appreciable change in the T_g upon changing the extent of quaternization (i.e. block incompatibility). Annealing at high temperatures followed by quenching at high rates caused no visible change in the DSC traces.

SAXA is useful for elucidating the structure of multiphase materials in the size range of about 2 - 200 nm. Both E-830 and E-1250 samples show very little scattering, and the intensity seems to reduce slightly with temperature. This is consistent with DSC data that both E-830 and E-1250 are almost single-phase materials. E-2000 sample shows much stronger scattering and the Bragg peak decreases with temperature. At 50 °C, the broad Bragg peak has a maximum at about $q = 0.47\ nm^{-1}$, which corresponds to a long spacing (*d*) of 13.5 nm; at high temperatures the peak is not sufficiently well-defined to allow determination of the long spacing with great confidence. The long spacing (*d*), was estimated from the position of the peak in the Lorentz-corrected scattered intensity vs. q data as $d = 2\pi / q_{\max}$. For E-3000 sample, a Bragg peak is clearly visible at 50 °C and decreases monotonically with temperature until it is barely visible as a shoulder at 120 °C. However, the same data after Lorentz correction show that the Bragg peak does not altogether vanish, even at the highest temperatures. The maximum in the scattering profile is between 0.4 and $0.42\ nm^{-1}$ at all temperatures, although the peak was found to be appreciably broader at high temperatures. This corresponds to a long spacing of 15.3 nm for E-3000 independent of temperature. We believed that E-3000 is above the MST at all the temperatures studied.

A comparison of the three I-series (I-725, I-1000 and I-2000) shows that long spacing increases with block length. Within each series, quaternization (i.e., block incompatibility) causes an increase in the scattering intensity in SAXS experiments, a decrease in peak width, and a decrease in the peak position, especially at low quaternization; the latter corresponds to an increase in the long spacing. This indicates that increasing incompatibility causes chain stretching.

High-temperature scattering experiments were also performed on these materials. All samples (except I-725-12, I-2000-0) showed no major change in scattering with temperature up to 130 °C, except for a slight increase in long spacing *d*. It should be noted that block incompatibility increases with decreasing temperature. The direction of the shift in *d* is consistent with the interpretation that, in block copolymers with polydisperse blocks, increasing incompatibility causes successively shorter blocks to microphase-separate and decrease *d*. However, the increasing incompatibility with quaternization contradicted this expectation by causing *d* to increase significantly. We have no explanation for this contradictory behavior upon increasing χ by decreasing temperature in one case and increasing quaternization in the other case. One possibility is that increasing quaternization has effects other than simply increasing block incompatibility.

Our SAXS scattering results also show the ambiguity of distinguishing between the "homogeneous" and the "microphase separate" states when the former has strong composition fluctuations and the latter has no long-range order. An order-disorder transition (ODT) is not meaningful for materials that lack long-range order, and it seems rather difficult to experimentally define a binodal curve separating the "homogeneous" and the "microphase separated" states. This view will be reinforced by the results of linear viscoelastic experiments discussed below.

Viscoelasticity

Both temperature and frequency sweep dynamic mechanical tests were performed on E-series polyurethanes. The rheological data for E-1250 show excellent superposition above 50°C giving a mastercurve that shows terminal (low frequency) behavior of $G' \alpha \omega^2$ and $G'' \alpha \omega$ which is characteristic of a viscoelastic liquid. For E-2000, this characteristic behavior is seen only above 80°C; below this temperature, time-temperature superposition (TTS) fails and the rheological curves seem to approach limiting slope that is much smaller than 2. The same feature is even more pronounced at a molecular weight of 3000 and TTS fails at even higher temperature. The frequency shift factors a_T for the three samples are coincident at high temperatures when the TTS is valid. The E1250 data fit well to the Williams-Landel-Ferry (WLF) equation with a reference temperature of 90°C. However, it must be borne in mind that there are two adjustable parameters to in the WLF equation. At lower temperatures, the shift factors show distinct deviations from the shift factors for E1250. Quantitative analysis showed that block length had a very large effect on the terminal properties of polyurethane melts with terminal viscosity varying as approximately (block length) $^{4.5}$. At sufficiently high temperature the polyurethanes had a relaxation spectrum similar to that of a homopolymer of low molecular weight, indicating that either the polyurethanes were homogeneous at high temperatures or microphase separation did not affect the relaxation spectrum. Finally, the shift factors at sufficiently high temperatures could be adequately represented by the WLF equation with "universal" values of the constants C_1g and C_2g, provided the reference temperature was taken to be the thermal Tg that the polyurethane would have if it were single phase.

In all I-series, increasing quaternization causes an increase in storage modulus at high temperatures and a correspondingly higher temperature for flow. This increasingly solid-like behavior with quaternization has three distinct causes that have been described briefly by Hamersky et al.. The first cause for the increasingly solid-like behavior is "bare" effects, i.e., those effects that are not related to microphase separation. In addition to the bare effects, the viscoelastic properties of the present materials are influenced by microphase separation in two qualitatively distinct ways. The first of these is important when one of the components has a much higher monomeric friction coefficient than the other. In such a case, microphase separation causes the local composition to deviate from the average composition, and hence the local monomeric friction coefficient also varies throughout the sample. This will be referred to as the "dynamic asymmetry" effect of microphase separation. The second effect of microphase separation is the "thermodynamic" aspect, which is the energy penalty of dragging a hard segment through the soft-segment-rich microphase, and vice versa. This energy penalty, which also impedes chain motion and thereby increases the viscosity, is independent of the relative friction coefficients of the two blocks.

At sufficiently high temperatures, TTS is seen to work for all materials in the experimental frequency range. The master curves may be described almost quantitatively using Rouse theory. In general, increasing quaternization is seen to increase both the terminal viscosity and the terminal relaxation time of polyurethanes. At lower temperatures, a failure of superposition is seen for materials with large block length or large block incompatibility. It is also observed that as quaternization increases, superposition fails at successively higher temperatures. Such failure of superposition has often been demonstrated to be due to an ODT or due to composition fluctuation. Since our SAXS experiments show almost no change with temperature, the failure of superposition of the cationomers cannot be attributed to microphase mixing. It is believed that this failure is due to proximity to the T_g of the hard-segment-rich microphase, because time-temperature superposition is not expected to apply so close to the T_g.

Finally, we also made two unusual observations: the apparent activation energy of terminal relaxation was independent of microphase separation and the terminal frequency response was liquid-like even for highly microphase separated polyurethanes. The first observation indicates that microphase separation in unentangled systems does not greatly hinder chain motion, in accordance with previous experimental results and theoretical expectations. The second observation that strongly contrasts the nonliquidlike terminal behavior of block copolymers with monodisperse blocks reiterates the role of the disordered nature of the microphase separated state in polyurethanes. Both of these observations indicate that the effects of microphase separation in polyurethanes are felt due to the large dynamic asymmetry, rather than an inability of the blocks to move through thermodynamically unfavorable regions.

Polyurethanes with hydrophobic soft segments for barrier applications

We have synthesized and tested more than twenty-five polyurethanes based on the soft segments of Table 3 and various hard segments such as 4',4-methylene bis(phenyl isocyanate) (MDI), 4',4-methylene bis(cyclohecyl isocyanate) (H_{12}MDI) and cyclohexane diisocyanate (CHDI). 1,4-butadiene was sued as a chain extender in every case. For those polyurethane block copolymers synthesized using HTPBD soft segments, post-synthesis hydrogenation was performed to saturate the soft segments. (These materials are designated as having h-HTPBD soft segments, to distinguish them from materials having pre-hydrogenated soft segments designated HTPE.) The hydrogenation was carried out chemically by *p*-toluenesulfonhydrazide. The FTIR study shows almost complete hydrogenation indicated by disappearance of peak at 965.7, 911.7, 722.7 cm^{-1} corresponding to wave number of 1,4-tans, 1,2-, and 1,4-cis absorption. We have elected to hydrogenate HTBP after incorporating it in the polyurethane since hydrogenation on the HTPB prepolymer may cause changes in the functionality. Hydrogenation causes no visible change in the amide double bond (~ 1500 cm^{-1}) indicating that the urethane linkage is not degraded during the hydrogenation reaction. This selective post-hydrogenation provides a new route to synthesize saturated polyurethanes since hydrogenation on the HTPBD prepolymer may cause changes in the functionality.

The mechanical properties of the polymers prepared in this study are compiled in Table 4. The moduli of the copolymers range from 4-50 MPa for materials with hard segment contents of 30% or less, and from 100-500 MPa for copolymers with hard segment content of ~40%. Ultimate elongations and strengths are in the range of 50-600% and 5-20 MPa, respectively. These properties are generally comparable to those that have been reported for other polyurethane copolymers with olefinic soft segments. However, higher ultimate elongations are achieved for the materials prepared in this study relative to those reported by other groups for materials of similar chemistry and preparation. The materials synthesized using the soft segment precursors provided by the Tudos group show a superior combination of high stiffness and high elongation relative to other materials prepared in this study and by others. In general, increasing hard segment contents leads to an increase in modulus and strength, but a decrease in ultimate elongations. The optimal hard segment content is between about 15% and 30%. A hard segment content significantly below or above these limits yield materials that are either too soft and weak or too brittle, respectively. A soft segment molecular weight of about 2000 is optimal for the desired mechanical properties. All samples are transparent at these hard segment contents even when a crystallizable hard segment such as MDI/BD is employed.

The barrier properties of these segmented, olefinic polyurethanes are also quite impressive. These elastomers were insoluble in all pure solvents tested, including aprotic solvents such as DMF and THF. The results of solvent immersion tests are compiled in Tables 5 and 6. The immersion tests showed low uptake of a small, polar solvent molecule (CH_3CN=acrylonitrile) by the HTPE and h-HTPBD urethanes, and moderate uptake of a chlorinated, aliphatic solvent. The lowest sorption numbers reported for 1,5-dichloropentane, in the range of 20-35%, are similar to those reported previously for cross-linked urethane systems with similar hard segment content. Even though there was considerable swelling of many of the materials by toluene, some high hard segment formulations were fairly resistant to this solvent, sorbing only moderate amounts (~35-50%) on extended immersion. For acrylonitrile and dichloropentane, diffusion coefficients of these polyurethanes are of on the order of 10^{-8} to 10^{-9} cm^2/s. These numbers rival those reported for elastomers and rubbers known to have the highest performance in barrier applications.

For polyurethane copolymers with hard segment content of ~30% or less, using H_{12}MDI as hard segment results in increased elastomeric character of the polymer, i.e., decreased strength and modulus and increased ultimate elongation. At higher hard segment contents, ~40%, the mechanical properties of the H_{12}MDI urethanes, including modulus, strength, and elongation, are superior to those of the MDI urethanes. The barrier properties of h-HTPBD and HTPE urethanes based on MDI are generally better than those based on H_{12}MDI since MDI hard segments can crystallize which will increase the chemical resistance.

The difference in branching content in soft segment was found to have a significant effect on mechanical and barrier properties of resulting polyurethanes. The branching content is highest in the Nippon Soda precursors (>80% vinyl), intermediate for the Japan Synthetic Rubber precursors (45-55% vinyl), and lowest for the Tudos materials (~15% vinyl). The packing in the Tudos and Nippon Soda materials should be correspondingly better than in the Japan Synthetic Rubber materials, due to the more uniform nature of the soft segment structure. This may account partially for the inferior mechanical performance of the Japan Synthetic Rubber urethanes. The low 1,2- vinyl branch content in the Tudos materials should lend this system the lowest free volume and best order in the soft segment regions, which may be the origin of the superior solvent resistance observed.

Our research showed that the sequence of soft segment hydrogenation versus urethane polymerization has an effect on properties as well. A comparison of the two polymers prepared from nearly identical Tudos precursors underscores the importance of this variable. The Tudos-HTPE-2136-24%HS urethane has both better mechanical properties and barrier properties relative to the Tudos-hHTPBD-1870-27%HS urethane, despite their similarity in formulation. Even though post-hydrogenation does not affect the urethane linkage, pre-hydrogenation of the soft segments may stabilize them to degradation during storage. Instability during storage may also account for the inferior performance of the urethanes prepared from Japan Synthetic Rubber precursors.

List of all publications and technical reports supported under this grant or contract.

1. Sachin Velankar and S.L. Cooper, "Microphase Separation and Rheological Properties of Polyurethane Melts. Part 1: Effect of Segment Length", *Macromolecules*, 31, 9891, 1998.

2. Sachin Velankar and S.L. Cooper, "Microphase Separation and Rheological Properties of Polyurethane Melts. Part 2: Effect of Block Incompatibility on the Microstructure", *Macromolecules*, 33(2), 382, 2000.

3. Sachin Velankar and S.L. Cooper, "Microphase Separation and Rheological Properties of Polyurethane Melts. Part 3: Effect of Block Incompatibility on the Viscoelastic Properties", *Macromolecules*, 33(2), 395, 2000.

4. Nora Beck Tan, Sharon Ma, Eugene Napadensky, James Sloan and Stuart Cooper, "Synthesis and Characterization of Transparent Barrier Urethanes Based on Polyethylene Soft Segments," Technical report for Army Research Lab, 2000

5. Sachin Velankar and S.L. Cooper, "Rheology and Microphase Separation in Polyurethanes and Polyurethane Ionomers", Poster Presentation, Conference of the American Institute of Chemical Engineers, Fall 1997.

6. Sachin Velankar and S.L. Cooper, "Melt Studies of Multiblock Polyurethane Elastomers", Conference of the American Physical Society, Spring 1997.

7. Nora Beck Tan, X.S. Ma, Jim Sloan, Gene Napadensky, Adam Frain, and S.L. Cooper, "Synthesis & Characterization of Transparent Barrier Urethanes Based on Polyethylene Soft Segments," APS Annual Meeting, Atlanta, GA, 4/99.

List of all participating scientific personnel showing any advanced degrees earned by them while employed on the project

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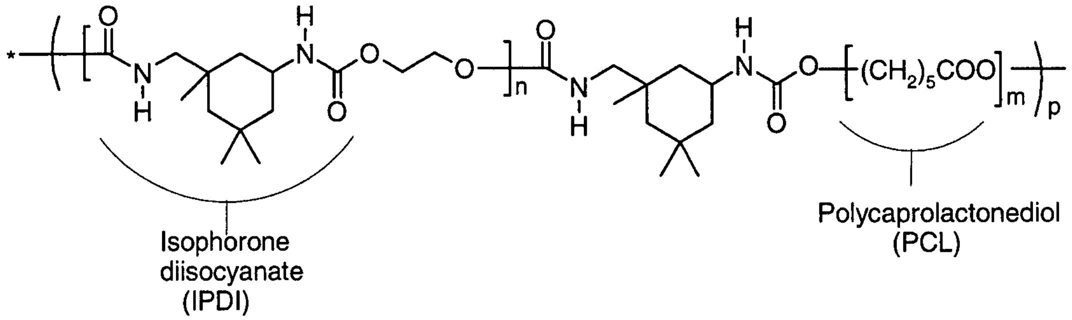
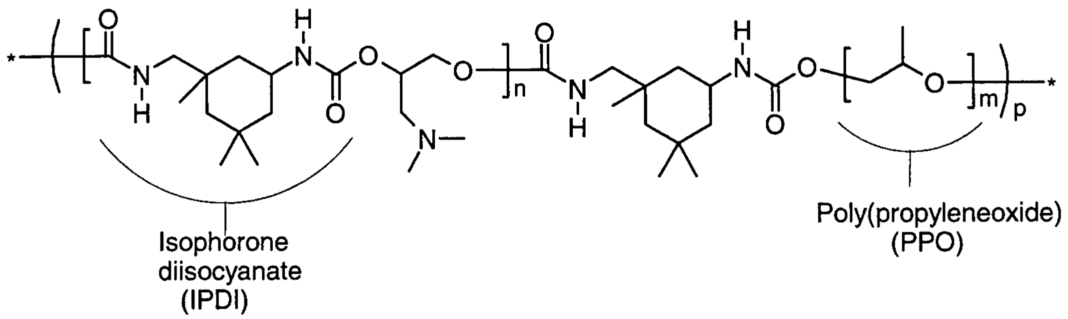
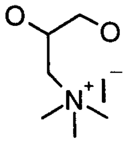
List of Figures and Tables



Polyesterurethanes: E-series





Dimethylamino-1,2-propanediol
(DMP) after quaternization

Polyurethane cationomers: I-series

Figure 1 **Structures of model polyurethanes**

Table 1 Thermal Properties of Polyesterurethane

Sample	Pure Homopolymer properties				Polyurethane properties		
	$T_{g,ss}$ °C	$\Delta C_{p,ss}$ J/g	$T_{g,hs}$ °C	$\Delta C_{p,hs}$ J/g	$T_{g,mid}$ °C	$T_{g,onset}$ °C	ΔC_p J/g
E-830	-75.5 ±1	0.21 ±0.03	36 ±2	0.43 ±0.05	-9 ±5	-33±3	0.43 ±0.02
E-1250	-71.5 ±1	0.17 ±0.03	36 ±2	0.43 ±0.05	-10 ±7	-45±3	0.40 ±0.07
E-2000	-67.0 ±1	0.15 ±0.01	36 ±2	0.43 ±0.05	--	-52±3	0.11 ±0.06
E-3000	-63.5 ±1	0.15 ±0.01	36 ±2	0.43 ±0.05	-52 ±2	-63±2	0.13 ±0.01

Table 2 Thermal Properties of Polyurethane Cationomers

Sample	Pure Homopolymer properties				Polyurethane properties	
	$T_{g,ss}$ °C	$\Delta C_{p,ss}$ J/g	$T_{g,hs}$ °C	$\Delta C_{p,hs}$ J/g	T_g °C	ΔC_p J/g
I725-0	-71.4 ±1	0.72 ±0.03	55 ±2	0.42 ±0.05	3.6	0.42
I725-12			56	0.38	3.2	0.38
I725-25			66	0.38	6.1	0.42
I725-40			78	0.38	3.9	0.45
I1000-0	-70.7 ±1	0.69 ±0.03	55 ±2	0.42 ±0.05	--	--
I1000-13			58	0.38	--	--
I1000-32			70	0.38	-33.1	0.124
I1000-40			80	0.38	-34.5	0.129
I2000-0	-69.2 ±1	0.66 ±0.03	55 ±2	0.42 ±0.05	-52.1	0.254
I2000-14			57	0.38	-55	0.242
I2000-29			66	0.38	-55	0.251

Table 3 Soft Segment Properties

Soft Segment Source	Initial State	M_n (g/mole)	PDI*	F_n	1,2 Content
Tudos	HTPBD	1245	1.34	1.62	15%
	HTPBD	1552	1.34	2.10	15%
	HTPBD	1870	1.62	1.90	17%
	HTPBD	5230	1.72	1.98	17%
	HTPE	2136	1.79	2.01	17%
Japan Synthetic Rubber	HTPBD	2000*	--	1.98[14]	43%
Nippon Soda	HTPE	1000*	--	--	--
	HTPE	2000*/2100[8,9]	1.5[8]	1.8[8,9]	82%[9]
	HTPE	3000*	--	--	--

*Reported by the manufacturer.

Table 4 Mechanical Properties of Polyurethanes with hydrophobic soft segment

Soft Segment (SS)	SS Source	SS M_n (g/mole)	Hard Segment (HS)	SS/HS/BD	% HS	Modulus (MPa)	UTS (MPa)	Elongation (%)
h-HTPBD	Tudos	1552	MDI	1/1/0	14	40.8	3.2	230
h-HTPBD	Tudos	1552	H_{12}MDI	1/1/0	14	2.4	0.4	350
h-HTPBD	Tudos	1245	MDI	1/4/3	40	486.2	32.8	150
h-HTPBD	Tudos	1870	MDI	1/3/2	27	50.3	6	57
h-HTPBD	Tudos	1870	MDI	1/6/5	39	279.3	24.6	105
h-HTPBD	Tudos	5260	MDI	1/5/4	18	5.8	7.9	431
HTPE	Tudos	2136	MDI	1/3/2	24	22.6	20.7	430
HTPE	Tudos	2136	H_{12}MDI	1/3/2	25	11.2	18.1	483
h-HTPBD	JSR	1970	MDI	1/3/2	26	12.5	8.9	227
h-HTPBD	JSR	1970	MDI	1/6/5	38	103.5	11.4	85
h-HTPBD	JSR	1970	H_{12}MDI	1/6/5	39	162	15	130
HTPE	NS	1000	MDI	1/1/0	19	1.6	4.7	43.5
HTPE	NS	1000	MDI	1/3/2	39	46.8	20.8	285
HTPE	NS	1000	H_{12}MDI	1/3/2	40	74.7	20.9	340
HTPE	NS	2000	MDI	1/2/1	20	3.8	8.9	561
HTPE	NS	2000	MDI	1/3/2	26	11.5	16	370
HTPE	NS	2000	H_{12}MDI	1/3/2	27	5.6	11.9	490
HTPE	NS	2000	MDI	1/6/5	38	42.1	26.4	270
HTPE	NS	3000	MDI	1/3/2	19	3.2	8.4	400

Table 5 Barrier Properties: Part A. Solvent Uptake

Soft Segment (SS)	SS Source	SS M_n (g/mole)	Hard Segment (HS)	% HS	CH_3CN* (%)	DCP (%)	Toluene (%)
h-HTPBD	Tudos	1245	MDI	40	6.41	34.50	35.20
h-HTPBD	Tudos	1870	MDI	27	4.58	46.7	111.6
h-HTPBD	Tudos	1870	MDI	39	--	23.5	--
h-HTPBD	Tudos	5260	MDI	18	3.11	87.9	210
HTPE	Tudos	2136	MDI	24	2.45	35.8	89.7
HTPE	Tudos	2136	$H_{12}MDI$	25	3.3	47.7	290.4
h-HTPBD	JSR	1970	MDI	26	41.03	--	196
h-HTPBD	JSR	1970	MDI	38	--	23.2	--
h-HTPBD	JSR	1970	$H_{12}MDI$	39	--	--	--
HTPE	NS	1000	MDI	19	4.47	--	273.2
HTPE	NS	1000	MDI	39	4.22	33.3	52.4
HTPE	NS	1000	$H_{12}MDI$	40	--	75.5	--
HTPE	NS	2000	MDI	20	2.71	--	216.2
HTPE	NS	2000	MDI	26	37.1	48.9	--
HTPE	NS	2000	$H_{12}MDI$	27	15.8	77.7	511.3
HTPE	NS	2000	MDI	38	9.52	32.5	50.28

*Acrylonitrile.

Table 6 Barrier Properties: Part B. Diffusion Coefficients

Soft Segment (SS)	SS Source	SS M_n (g/mole)	Hard Segment	% HS	D CH_3CN (cm^2/s)	D DCP (cm^2/s)	D Toluene (cm^2/s)
h-HTPBD	Tudos	1245	MDI	40	1.49E-08	--	5.11E-08
h-HTPBD	Tudos	1870	MDI	27	4.41E-08	--	3.63E-08
h-HTPBD	Tudos	1870	MDI	39	--	--	--
h-HTPBD	Tudos	5260	MDI	18	8.46E-08	--	5.14E-08
HTPE	Tudos	2136	MDI	24	5.30E-08	--	3.00E-07
HTPE	Tudos	2136	$H_{12}MDI$	25	1.80E-08	6.13E-08	4.10E-07
h-HTPBD	JSR	1970	MDI	26	--	--	--
h-HTPBD	JSR	1970	MDI	38	--	--	--
h-HTPBD	JSR	1970	$H_{12}MDI$	39	--	--	--
HTPE	NS	1000	MDI	19	1.49E-08	--	2.01E-07
HTPE	NS	1000	MDI	39	3.01E-08	2.98E-08	3.20E-07
HTPE	NS	1000	$H_{12}MDI$	40	--	--	--
HTPE	NS	2000	MDI	20	1.32E-08	--	1.41E-07
HTPE	NS	2000	MDI	26	3.13E-09	--	--
HTPE	NS	2000	$H_{12}MDI$	27	2.98E-09	--	2.53E-07
HTPE	NS	2000	MDI	38	--	--	--