

Mechanical and Thermal Properties of UV-Curable Polyurethane and Polyurea Acrylates

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SYNOPSIS

Soft-segment molecular weight, soft-segment crystallization, hard-segment-type, and reactive diluent level were examined in urea and urethane acrylates. Increasing soft-segment molecular weight led to a decreased tensile modulus, increased strength, and increased elongation at break. Soft-segment crystallization increased the modulus below the melting temperature, but decreased the modulus above the melting temperature because crystallization interfered with cross-linking. Materials with hard segments that allowed for greater phase separation showed a higher modulus, higher ultimate stress, and higher ultimate elongation. Materials with reactive diluents 2-hydroxyethyl methacrylate (HEMA) and *N*-vinyl pyrrolidinone (NVP) showed qualitatively different behavior. HEMA caused the modulus and strength to increase with little effect on elongation up to concentrations of 50 wt %; at higher concentrations, the elongation decreased. NVP also increased the modulus and strength; however, at 40 wt % NVP, ultimate elongation increased in a well-phase-separated system and decreased in a poorly phase-separated system. In tensile tests, samples with 40% NVP also showed substantial sample necking and drawing. © 1993 John Wiley & Sons, Inc.

I. INTRODUCTION

Interest in UV-curable polymer systems is extremely high, as evidenced by recent books,^{1,2} patents,³⁻⁵ and numerous other publications. UV-curing provides a simple way to produce a stiff cross-linked polymer without any solvent, which eliminates a potential waste stream. Applications involving UV-curable materials include thin-film coatings, adhesives, and photolithography. An important subset of UV-curable materials are urethane acrylates, which typically contain a polyester or polyether diol of molecular weight 1000–5000 tipped with a diisocyanate at each end. The second isocyanate linkage of the diisocyanate is reacted with a small molecule that contains the acrylate functionality. To this UV-curable oligomer, a reactive diluent may be added to lower the viscosity of the prepolymer. Reactive dil-

uents are small molecules that also contain acrylate functionality. At this point, the oligomer-diluent mixture is a liquid, which allows for pouring into molds, spreading on surfaces, etc. With the addition of UV-sensitive photoinitiators and catalysts, exposure to UV light causes the material to harden in a matter of seconds or, at most, minutes to a highly cross-linked, thermally and chemically stable material. Urethane acrylates are especially important because of the toughness, abrasion resistance, and flexibility that may be achieved with these materials.

A number of factors influence the mechanical and thermal properties of these materials. Oraby and Walsh^{6,7} investigated the effect of a reactive diluent on the tensile properties of a urethane acrylate with an ethylene glycol/adipic acid alternating copolymer soft segment and a toluene diisocyanate (TDI) hard segment tipped with 2-hydroxyethyl methacrylate (HEMA). Most reactive diluents caused an increase in modulus along with little change in the ultimate mechanical properties. One diluent, *N,N'*-diethylaminoethyl acrylate (DEAEA), substantially improved the ultimate properties to a level almost equivalent to linear polyurethanes. The authors be-

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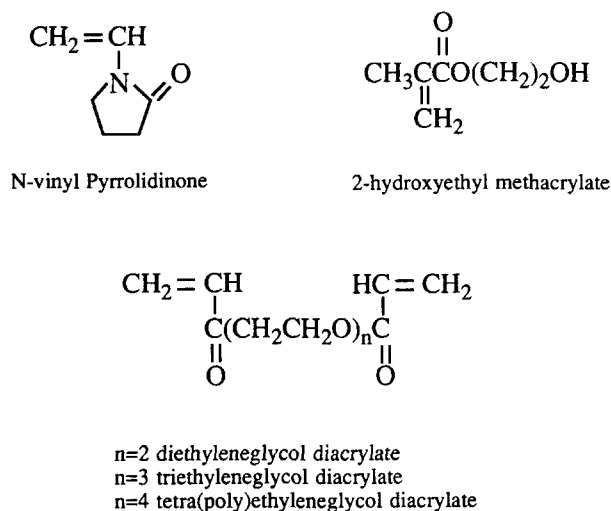


Figure 1 Structures of reactive diluents.

lieved that DEAEA was acting as a chain-transfer agent to substantially reduce the cross-link functionality.

The effect of a reactive diluent was also studied extensively in this laboratory. Diluent structures are shown in Figure 1. Koshiba et al.⁸ studied the effect of 0–25% diluent content on urethane acrylates based on a poly(tetramethylene oxide) (PTMO) soft segment and either a TDI or isophorone diisocyanate (IPDI) hard segment. The diluents studied

were *N*-vinyl pyrrolidinone (NVP) and diethylene glycol diacrylate (DEGDA). Both diluents increased the Young's modulus and ultimate tensile strength. The effect on the ultimate elongation depended on the phase separation of the materials. For two-phase materials, NVP increased the ultimate elongation slightly, whereas for one-phase materials, the elongation at break dropped substantially. In both cases, DEGDA decreased the ultimate elongation. The reactive diluent was found to lower the prepolymer viscosity substantially.

Speckhard et al.⁹ studied the effect of a reactive diluent on PTMO/TDI materials. Four reactive diluents were studied: NVP, DEGDA, triethyleneglycol diacrylate (TEGDA), and tetra-(poly[ethylene glycol diacrylate]) (PEGDA). Diluent levels studied were 0–40%. Dynamic mechanical thermal analysis (DMTA) and differential scanning calorimetry (DSC) were used to assess phase separation. Soft-segment molecular weight was the most important factor controlling phase separation. Increasing the reactive diluent concentration increased phase separation. The diluent was preferentially incorporated into the hard-segment phase. All the diluents used increased the ultimate stress and modulus and decreased the ultimate elongation.

The hard-segment type has also been studied. Hard-segment structures are shown in Figure 2.

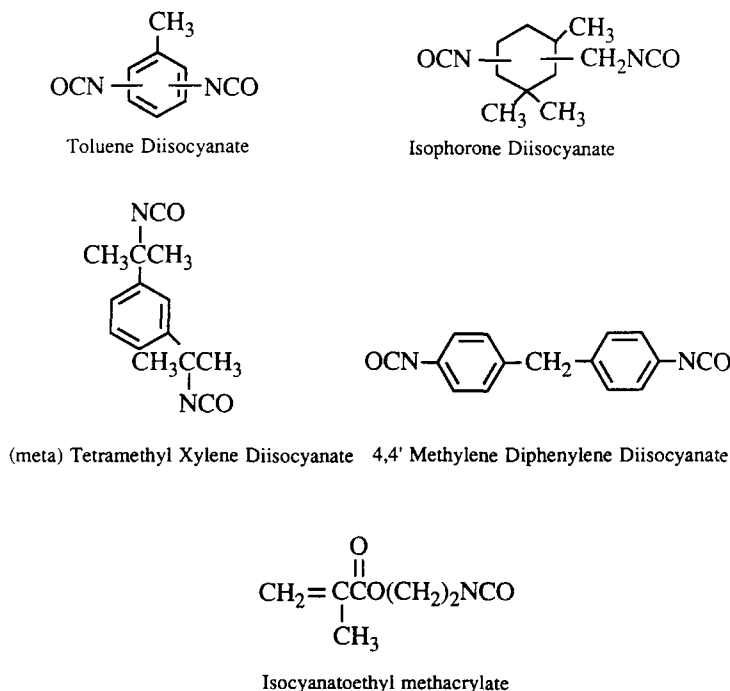


Figure 2 Isocyanate containing hard segments.

Koshiba et al.⁸ compared TDI and IPDI hard segments and found little difference in mechanical properties. IPDI and 4,4'-methylene diphenylene diisocyanate (MDI) were compared in materials with poly(tetramethylene adipate) soft segments by Li et al.¹⁰ The higher hard-segment content of the MDI-based materials (MDI has two aromatic rings, whereas IPDI has one cyclohexane ring) led to a higher modulus and stress at break, whereas the effect on elongation at break was negligible.

Isocyanatoethyl methacrylate (IEM) contains an isocyanate group and a methacrylate group on the same molecule. PTMO-based materials tipped with this molecule showed substantially lower extensibility than the materials discussed previously.⁹ DMTA spectra of IEM materials indicated that phase separation in these systems was poor. Addition of NVP increased the modulus and strength substantially. In a study by Nakazoto et al.,¹¹ TDI-hydroxyethyl acrylate endgroups were compared to an acryloyl chloride endgroup in materials with polybutadiene soft segments. The mechanical properties of the acryloyl chloride-based material were reduced, which the authors attributed to a lack of hydrogen bonding. This result may also have been due to decreased phase separation; however, no DMTA or DSC spectra of these materials were given in the article.

Soft-segment type and molecular weight are the two variables most extensively investigated in the urethane acrylate family of materials. Oligomers investigated include polycarbonates,^{9,12} poly(propylene oxide),¹² poly(tetramethylene oxide),^{8,9,12} polycaprolactone,^{8,12} poly(dimethylsiloxane),^{13,14} ethylene glycol/adipic acid,^{6,7} poly(tetramethylene adipate),¹⁰ and polybutadiene.¹¹ Oligomer type and molecular weight have been found to have a substantial effect on mechanical properties. As the molecular weight of the soft segment decreases, ultimate elongation decreases and tensile strength increases. The first effect has been attributed to longer distances between cross-links, whereas the second has been attributed to an increase in the hard-segment weight fraction. Polyol type affects the modulus but does not affect the ultimate elongation.

Much less work has been done on urea acrylates. In an article by Noren et al.,¹⁵ urethane acrylates were compared to urea acrylates. Urea groups had only a slight effect on the mechanical properties. The modulus was slightly greater for the urea material, while the ultimate properties were slightly lower. Nothing in that study suggested that trends seen in urethane acrylates would not be followed in urea acrylates as well.

In this study, a total of 25 different materials was synthesized. Two soft-segment types were studied: polycaprolactone (PCL) and benzylamine-terminated PTMO (Polamine®). The effect of soft-segment molecular weight, soft-segment crystallization, hard-segment type, and diluent content on physical properties was investigated. Prepolymer viscosity, DSC, tensile testing, and DMTA were used to characterize the materials.

II. EXPERIMENTAL

Materials and Synthesis

Poly(caprolactone diol) (PCL) was obtained from the Aldrich Chemical Co. Polamine (POL) was obtained from the Air Products Corp. Oligomer structures are shown in Figure 3. PCL was dried for (24 h) at 70°C under vacuum prior to use. TDI, IPDI, and TMXDI were purchased from Aldrich. IEM was kindly provided by M. R. Thomas of the Dow Chemical Corp. and the purity was greater than 99%.¹⁶ HEMA and NVP were purchased from Aldrich. Dibutyl tin dilaurate (DABCO® T12) catalyst was purchased from Air Products. The initiator, 2,2-diethoxyacetophenone (DEAP), was purchased from Polysciences.

The oligomer was initially charged to a 60 mL jar. The isocyanate and 0.1 wt % of the T-12 catalyst were added to the PCL oligomer. For the POL oligomer, the catalyst was added at the time of the HEMA addition. The jar was shaken for approximately 5 min, then the mixture was transferred to a 65°C convection oven for 1 h. When diisocyanates were used, HEMA was then added. The mole ratio of the oligomer:isocyanate compound : HEMA was 1 : 2 : 2. After addition of the HEMA, the mixture was stored at 65°C for 3 h and then allowed to cool in air to room temperature and was stored at room temperature overnight. The reaction of the IEM

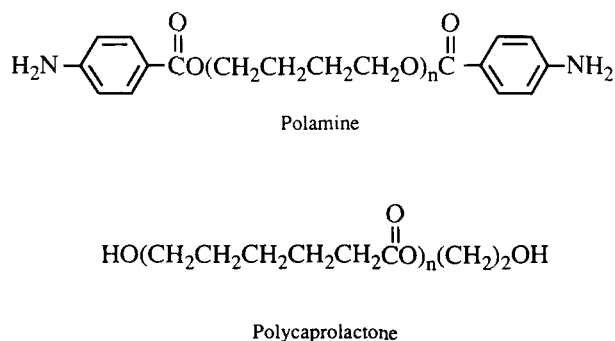


Figure 3 Structures of oligomers.

with oligomer also took place at 65°C for 1 h. The prepolymer was then cooled to room temperature and stored overnight. The mol ratio of the oligomer : IEM was 1 : 2.

Immediately prior to curing, 0.6 wt % DEAP was added along with the diluent. The sample was mixed thoroughly to ensure a homogeneous system. Approximately 1 mm-thick films with a radius of 5 cm were cast onto mylar transparency films. The prepolymer-diluent mixture was cast at approximately 50°C. The films were cured under 20 W mercury lamps for 30 min; each side faced the lamps for 15 min. The films were postcured at 70°C in a vacuum oven for 24 h, followed by storage in a desiccator. For PCL systems with low diluent content, the material crystallized during curing; therefore, the films were placed on a hot plate during curing to prevent crystallization. Unless otherwise noted, all films were noncrystalline as measured by DSC.

Sample Designation

An example sample designation is POL-2000-IPDI-HEMA-NVP-20. The first three letters designate the soft segment (PCL or POL) followed by the soft-segment molecular weight, hard segment, vinyl group, and, finally, reactive diluent type and weight percent reactive diluent. The weight percent of the diluent is based on the total weight after adding the reactive diluent. Table I lists all the samples used in this study.

Characterization Methods

(1) Viscosity

Viscosity measurements were made of the prepolymer immediately prior to casting. Measurements

were made on a Brookfield RVT viscometer equipped with a #21 small sample adapter. Calibration curves supplied by Brookfield were checked with viscosity standards. This adapter allowed for temperature control, which was accomplished through a recirculating waterbath. All measurements were made at 50°C.

(2) Stress-Strain

Uniaxial stress-strain measurements were made with a table model Instron at room temperature using a crosshead speed of 0.5 in./min. Samples were cut from cured films using an ASTM D1708 die. All measurements represent the average of three runs. The engineering stress was calculated based on the initial area of the sample.

(3) Differential Scanning Calorimetry

DSC measurements were made on a Perkin-Elmer DSC 2 equipped with a 3500 series data station or a Perkin-Elmer DSC 7 with a 7500 series data station. Temperature calibration was via mercury and indium standards. Indium was used to calibrate enthalpy measurements. The measurements were performed under a helium purge at a heating rate of 20°C/min.

Glass transition temperatures were determined via the following method: Lines were drawn along the approximately linear DSC trace above and below the glass transition. A third line was drawn corresponding to the slope at the inflection point of the glass transition. The glass transition temperature was calculated as the average of intersection points between the third line and the two other lines. The heat-capacity change was calculated from two intersection points as well.

Table I Samples Synthesized for this Study

Polamine-based Materials	Polycaprolactine-based Materials
POL-2000-IEM	PCL-3000-TDI-HEMA
POL-2000-TDI-HEMA	PCL-3000-TDI-HEMA-HEMA-20
POL-2000-IPDI-HEMA	PCL-3000-IPDI-HEMA CRYSTALLIZED
POL-2000-IPDI-HEMA-NVP-20	PCL-3000-IPDI-HEMA
POL-2000-IPDI-HEMA-NVP-40	PCL-3000-IPDI-HEMA-HEMA-20
POL-2000-IPDI-HEMA-NVP-50	PCL-3000-IPDI-HEMA-HEMA-40
POL-2000-TMXDI-HEMA	PCL-2000-IPDI-HEMA
POL-2000-TMXDI-HEMA-NVP-20	PCL-2000-IPDI-HEMA-HEMA-20
POL-2000-TMXDI-HEMA-NVP-40	PCL-2000-IPDI-HEMA-HEMA-40
POL-2000-IEM	PCL-2000-IPDI-HEMA-HEMA-50
POL-808-IEM	PCL-2000-IPDI-HEMA-HEMA-60
POL-808-IEM-NVP-20	PCL-2000-IPDI-HEMA-HEMA-70
POL-808-IEM-HEMA-20	PCL-2000-TMXDI-HEMA-HEMA-20
	PCL-2000-TMXDI-HEMA-HEMA-40

(4) Dynamic Mechanical Thermal Analysis

A Rheometrics RSA II in the tension mode was used to acquire DMTA spectra. Samples were cut using an ASTM D1043 die with the ends cut to the proper length. The approximate test dimensions were $23 \times 6.3 \times 1$ mm. The Autotension mode was used with a 120% force for pretension. Three-degree temperature steps with a 0.1 min soak time was used. It was found that increasing the soak time to 1 min did not affect the spectra. The frequency of testing was 16 Hz. The temperature range tested was -150 to 300°C ; however, the samples often would break between 200 and 300°C . DSC results indicated that significant sample degradation occurred in this temperature range.

III. RESULTS AND DISCUSSION

Viscosity

Table II shows the viscosity for selected samples. Because of the wide range of viscosities, a number of different shear rates were necessary to keep within the range of the instrument. A least-squares fit to the power law¹⁷ was used if necessary to extrapolate the viscosity to 1 s^{-1} . The power law is shown below:

$$\eta = m\dot{\gamma}^{n-1} \quad (1)$$

η is the measured viscosity; $\dot{\gamma}$, the shear rate; and n and m , empirically determined parameters for a particular system. For a Newtonian fluid, $n = 1$ and m is the viscosity.

For all the systems listed in Table II, the value of n was between 0.94 and 1.0, which indicates a fluid that was almost Newtonian. As Table II shows, the diluent dramatically lowers the viscosity. A 20% increase in diluent content lowers the viscosity by approximately an order of magnitude. Hard-segment

Table II Viscosity of Prepolymers at 1 s^{-1}

Material	Viscosity (cp)
PCL-2000-IPDI-HEMA	46,500
PCL-2000-IPDI-HEMA-HEMA-20	2,430
PCL-2000-IPDI-HEMA-HEMA-40	525
PCL-2000-IPDI-HEMA-HEMA-50	230
PCL-2000-TMXDI-HEMA-HEMA-20	2,500
PCL-2000-TMXDI-HEMA-HEMA-40	500
PCL-3000-IPDI-HEMA-HEMA-20	5,200
PCL-3000-IPDI-HEMA-HEMA-40	850
POL-2000-TMXDI-HEMA-NVP-20	1,180
POL-2000-IPDI-HEMA-NVP-40	270

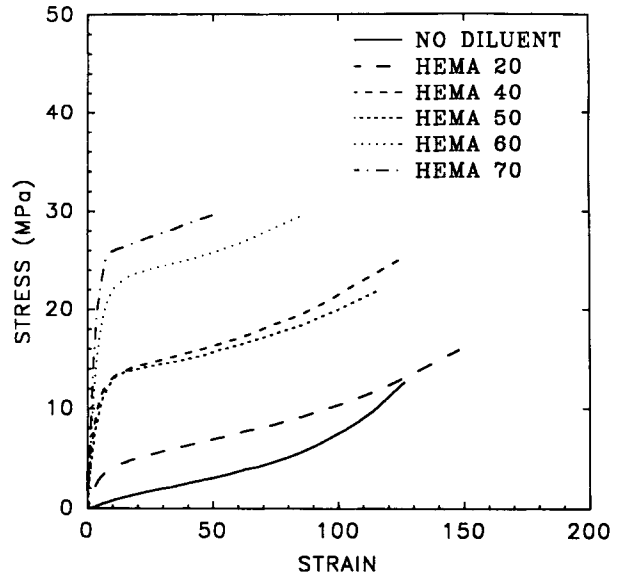


Figure 4 Effect of diluent level on the stress-strain curve in PCL-2000-IPDI-HEMA-HEMA- x .

type does not seem to affect the viscosity substantially. Lin et al.¹² noted that an increase in soft-segment molecular weight increases the viscosity of the prepolymer and the same trend is observed here.

Effect of Diluent Level on Cured Films

Besides lowering the prepolymer viscosity, diluent content has a large effect on mechanical and thermal properties. Figure 4 shows the stress-strain curve for the PCL materials, whereas Figure 5 shows the same curve for the POL materials. Table III lists the tensile results for all materials tested in this

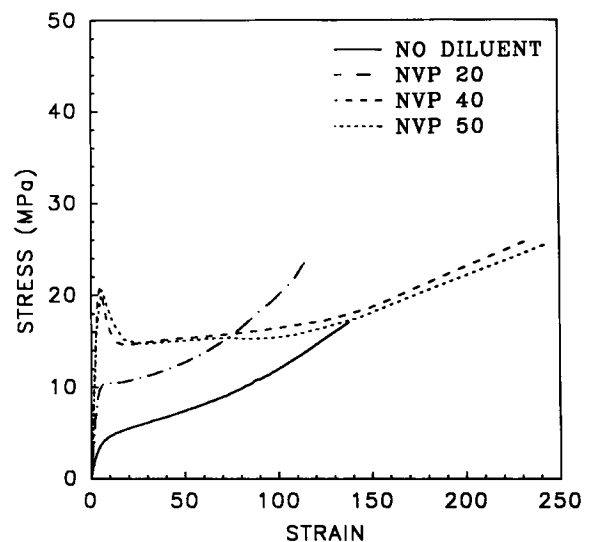


Figure 5 Effect of diluent level on the stress-strain curve in POL-2000-IPDI-HEMA-NVP- x .

Table III Tensile Properties of Urethane Acrylates

Material	Modulus (MPa)	Ultimate Elongation	Ultimate Stress (MPa)
POL-2000-IPDI-HEMA	110.0	125	16.5
POL-2000-IPDI-HEMA-NVP-20	324.0	115	23.8
POL-2000-IPDI-HEMA-NVP-40	623.0	230	25.5
POL-2000-IPDI-HEMA-NVP-50	572.0	240	25.5
POL-2000-TMXDI-HEMA	15.5	100	6.2
POL-2000-TMXDI-HEMA-NVP-20	372.0	70	11.4
POL-2000-TMXDI-HEMA-NVP-40	875.0	20	17.2
POL-2000-TDI-HEMA	51.7	110	12.8
POL-2000-IEM	9.3	36	4.5
POL-650-IEM	227.0	20	18.3
POL-650-IEM-NVP-20	903.0	18	30.3
POL-650-IEM-HEMA-20	598.0	31	21.4
PCL-3000-IPDI-HEMA	8.6	245	15.7
PCL-3000-IPDI-HEMA-HEMA-20	66.5	235	22.0
PCL-3000-IPDI-HEMA-HEMA-40	226.8	205	25.5
PCL-2000-IPDI-HEMA	6.2	125	12.8
PCL-2000-IPDI-HEMA-HEMA-20	75.1	150	16.2
PCL-2000-IPDI-HEMA-HEMA-40	438.0	125	25.5
PCL-2000-IPDI-HEMA-HEMA-50	324.0	115	22.1
PCL-2000-IPDI-HEMA-HEMA-60	537.0	85	30.3
PCL-2000-IPDI-HEMA-HEMA-70	690.0	52	30.3
PCL-2000-TMXDI-HEMA-HEMA-20	58.6	145	11.7
PCL-2000-TMXDI-HEMA-HEMA-40	296.0	125	18.2
PCL-3000-IPDI-HEMA CRYST	88.9	170	15.7

study. In all cases, increasing diluent content caused an increase in the modulus and ultimate stress.

The behavior of the POL-IPDI materials with NVP was extremely interesting. At 40 and 50% diluent level, the elongation at break was a factor of two higher than for the material without diluent. Because of this unexpected result, the synthesis was repeated and the result was essentially the same. As Figure 5 shows, the behavior of the films with high NVP content was qualitatively different in the tensile test compared to other materials in this study. Films with high NVP content showed substantial necking and drawing during the test.

The PCL-based materials with HEMA diluent showed increases in both modulus and ultimate stress. However, the ultimate elongation did not change significantly up to 50% diluent content. At higher diluent contents, the elongation at break decreased. The modulus enhancement was much greater for this material than for the POL material, primarily because the modulus without any diluent was an order of magnitude lower for the PCL material. The ultimate stress reached a plateau as the diluent content increased for both the PCL and POL materials.

Two factors could explain the rise in modulus: The diluent, which upon curing becomes part of a glassy phase, may have been acting as a filler. The Guth-Smallwood equation¹⁸ quantifies this effect:

$$\frac{E_f}{E_0} = 1 + 2.5V_f + 14.1V_f^2 \quad (2)$$

where V_f is the volume fraction of the filler. For V_f of 0.2, the increase in modulus is predicted to be slightly greater than a factor of 2, and for V_f of 0.4, the increase in modulus is predicted to be a factor of 4.25. This is slightly below the increase for the POL materials and significantly below the increase for the PCL material.

The diluent may have also increased cross-link functionality. The phantom network theory^{19,20} predicts that the modulus E will be given by

$$E = 3\left(\frac{f-2}{f}\right)\nu RT \quad (3)$$

where f is the cross-link functionality; ν , the cross-link density; R , the gas constant; and T , the temperature. The addition of the diluent may have al-

lowed higher functionality cross-links to form either through some reactivity effect or through an increase in chain mobility caused by a decrease in viscosity. The cross-link density may have increased as well since a junction where only two chains had been connected could have become a junction where three or more chains were connected, which would be reflected in the above equation by an increase in the cross-link density. Since the increase in modulus for the PCL materials was significantly greater than for the POL materials, an increase in functionality or an increase in cross-link density was probably much more important for the PCL materials.

DSC traces showed only a soft-segment glass transition temperature at about -55°C for the PCL-based materials and about -75°C for the POL-based materials. The absence of a hard-segment glass transition was not surprising; no transition was noticeable in DSC traces of similar systems previously studied. PCL-2000-IPDI-HEMA-HEMA-40 also possessed an extremely small melting endotherm, corresponding to PCL crystallites. Table IV lists the heat-capacity change and temperature associated with the glass transition for all the samples in this study. The heat-capacity change decreased as the diluent content increased, consistent with the soft-

segment phase weight fraction decreasing. Either the diluent was forming its own phase or was partitioning into the hard-segment phase. The soft-segment phase purity for the PCL material did not change (except perhaps for the 70% HEMA material) as indicated by the consistency of T_g . For the POL materials, addition of the diluent caused only a slight drop in the soft-segment glass transition temperature.

The change in the storage modulus E' showed the same trends as did Young's modulus, namely, the value increased as the diluent content increased. E' and E'' are shown in Figure 6(a) and (b) for the PCL-based materials, in Figure 7(a) and (b) for the POL-IPDI-based materials, and in Figure 8(a) and (b) for the POL-TMXDI-based materials. Increasing the diluent content decreased the magnitude of the soft-segment glass transition E'' peak at -50°C ; however, the position remained relatively constant. These results confirmed the conclusions drawn from the DSC data. Loss of intensity in the E'' peak resulted from a decreased weight fraction of the soft segment, whereas constancy in T_g indicated little change in the purity of the soft-segment phase.

As the diluent content increased, the hard-segment glass transition occurred at higher tempera-

Table IV Differential Scanning Calorimetry Data for Urethane Acrylates

Material	Glass Transition Temperature ($^{\circ}\text{C}$)	Heat-Capacity Change (J/G K)
POL-2000-IPDI-HEMA	-75	0.25
POL-2000-IPDI-HEMA-NVP-20	-78	0.18
POL-2000-IPDI-HEMA-NVP-40	-79	0.12
POL-2000-IPDI-HEMA-NVP-50	-82	0.09
POL-2000-TMXDI-HEMA	-74	0.26
POL-2000-TMXDI-HEMA-NVP-20	-78	0.16
POL-2000-TMXDI-HEMA-NVP-40	-84	0.08
POL-2000-TDI-HEMA	-74	0.28
POL-2000-IEM	-78	0.36
POL-650-IEM	-40	0.07
POL-650-IEM-NVP-20	-41	0.09
POL-650-IEM-NVP-40	-34	0.10
PCL-3000-IPDI-HEMA	-56	0.29
PCL-3000-IPDI-HEMA-HEMA-20	-56	0.22
PCL-3000-IPDI-HEMA-HEMA-40	-55	0.20
PCL-2000-IPDI-HEMA	-52	0.38
PCL-2000-IPDI-HEMA-HEMA-20	-54	0.25
PCL-2000-IPDI-HEMA-HEMA-40	-52	0.17
PCL-2000-IPDI-HEMA-HEMA-50	-54	0.16
PCL-2000-IPDI-HEMA-HEMA-60	-56	0.07
PCL-2000-IPDI-HEMA-HEMA-70	-60	0.07
PCL-2000-TMXDI-HEMA-HEMA-20	-51	0.21
PCL-2000-TMXDI-HEMA-HEMA-40	-53	0.14
PCL-3000-IPDI-HEMA CRYST	-52	0.19

tures for both the PCL and POL materials. No evidence existed in the DMTA spectra for a third phase, except when the materials were exposed to air, as discussed later. The diluent preferentially segregated to the more polar hard phase, without changing soft-segment phase purity. This conclusion agrees with the results of Speckhard et al.⁹

The POL-TMXDI material showed qualitatively different behavior in tensile tests than that of POL-IPDI as the diluent content increased. As shown in Figure 9, the ultimate elongation decreased substantially as the NVP diluent content increased. As noted in the Introduction, Koshiba et al.⁸ noticed that NVP lowered ultimate elongation in one-phase photopolymerizable urethane acrylate materials.

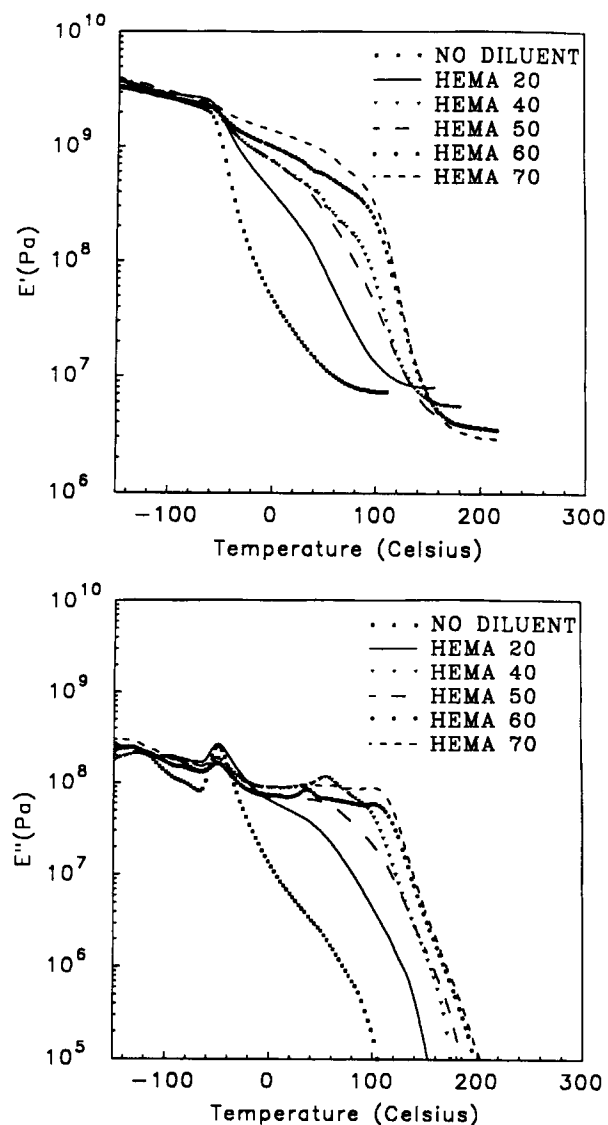


Figure 6a and 6b: Effect of diluent level on DMTA spectra for PCL-2000-IPDI-HEMA-HEMA-x: (a) E' ; (b) E'' .

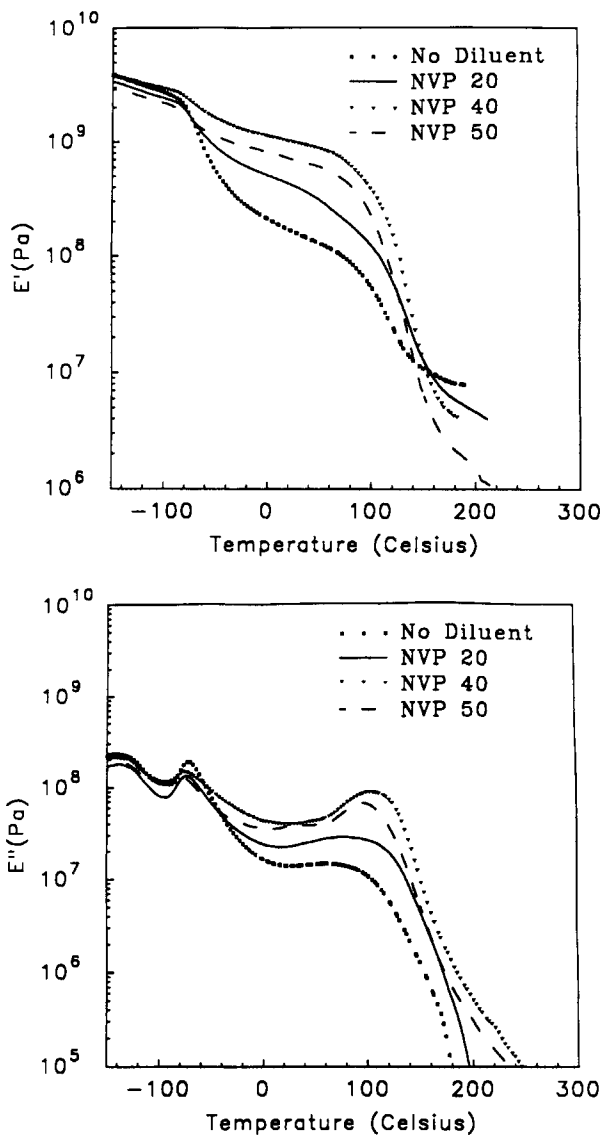


Figure 7a and 7b: Effect of diluent level on DMTA spectra for POL-2000-IPDI-HEMA-NVP-x: (a) E' ; (b) E'' .

DMTA spectra suggest that the hard-segment phase was less cohesive in POL-TMXDI materials since the E' vs. temperature curves fell off much more rapidly after the soft-segment glass transition temperature. Therefore, the qualitatively different behavior of the POL-TMXDI material was probably due to a more contaminated hard-segment phase that did not allow NVP to reinforce the hard phase.

Both the heat-capacity change and the temperature of the glass transition were almost identical between the POL-TMXDI and the corresponding POL-IPDI materials, which indicates that the soft-segment phase purity was essentially identical even though the hard-segment phase was substantially different. Assuming that the hard-segment phase

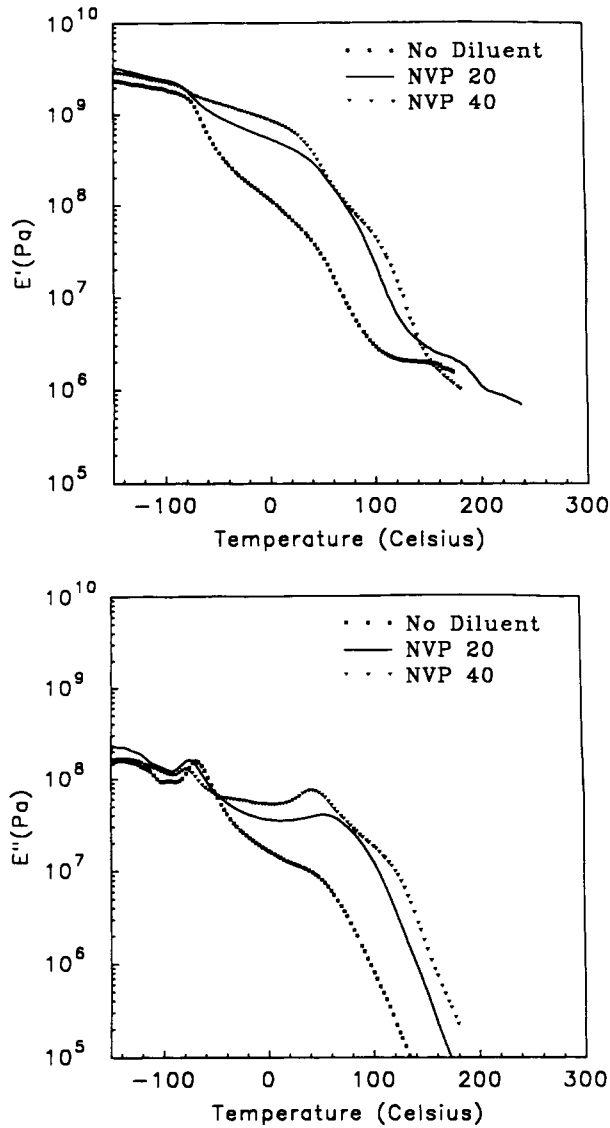


Figure 8 Effect of diluent level on DMTA spectra for POL-2000-TMXDI-HEMA-NVP-*x*: (a) E' ; (b) E'' .

included significantly more soft segment in POL-TMXDI, the soft-segment heat-capacity change should have been less in the POL-TMXDI materials. A smaller heat-capacity change was evident at 40% NVP for POL-TMXDI; however, this was not the case in the NVP-20 and the material containing no diluent. For the lower diluent material, not as much dispersed soft segment would be required to disrupt the hard-segment domains; perhaps, the amount required was too small to noticeably affect the heat-capacity change of the soft-segment transition.

Exposure to air changes the properties of these materials. A film of POL-2000-IPDI-HEMA-NVP-40 was synthesized and a DMTA spectrum was immediately collected. Then, the film was exposed to

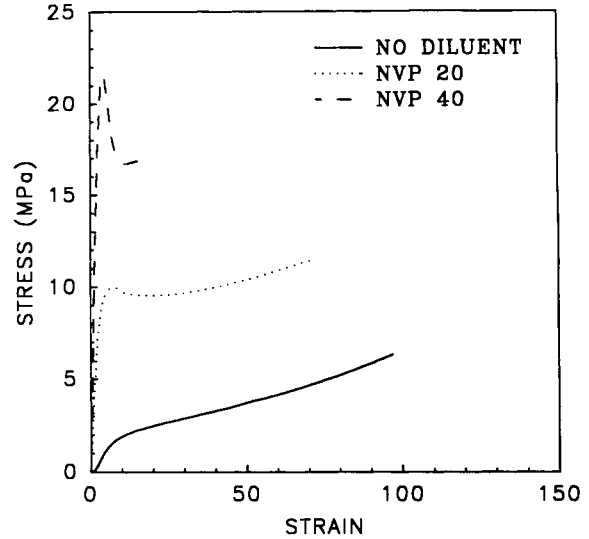


Figure 9 Effect of diluent level on the stress-strain curve in POL-2000-TMXDI-HEMA-NVP-*x*.

air at room temperature for 3 weeks and another DMTA spectrum was collected. The results are shown in Figure 10. DMTA spectra indicate the formation of a third phase with a transition at about 50°C. Both HEMA and NVP are hygroscopic, NVP more so than HEMA. Water vapor is being absorbed from the air and this transition may be due to a plasticized NVP phase.

Effect of Hard-segment Type on Cured Films

Hard-segment type had a significant influence on the tensile properties of the material, as shown in

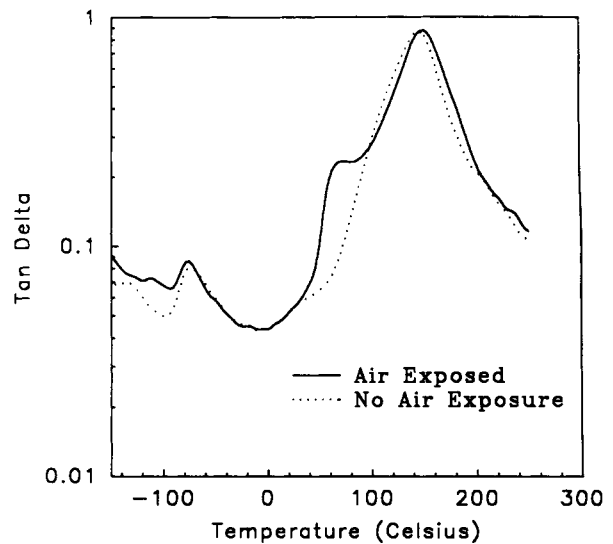


Figure 10 Effect of 3 weeks exposure to air on tan delta for POL-2000-IPDI-HEMA-NVP-*x*.

Figure 11. This effect was investigated with materials based on a POL-2000 soft segment with no diluent. IPDI-based materials had the highest modulus and strength; TDI was slightly inferior to IPDI. TMXDI showed reduced tensile properties; as discussed previously, this seems to be a result of a more contaminated hard-segment phase.

Materials synthesized with IEM showed markedly inferior tensile properties. The elongation, modulus, and stress at break were all lower than those of the other isocyanates studied. The soft-segment glass transition temperature as measured by DSC for the IEM materials was 3°C less than for those containing the other hard segments. Rather than resulting from improved phase separation, this result might indicate that hard segments do not restrict the mobility of the soft segment as well in the IEM-based materials. The change in heat capacity during the glass transition was slightly higher for the IEM-based materials. This could indicate less soft segment dissolved in the hard segment or could result from more hard segment dissolved in the soft segment.

DMTA curves [Fig. 12(a) and (b)] support the conclusion that the IEM-based material showed little phase separation. The plateau modulus was very flat for the IEM sample in the region 0–200°C, which is similar to simple one-phase cross-linked rubbers. Although IEM does not contain a 6-membered carbon ring as the other compounds do, Polamine is encapped with an aromatic ring that could allow for phase separation. However, in this system, phase separation, if it did occur, was marginal.

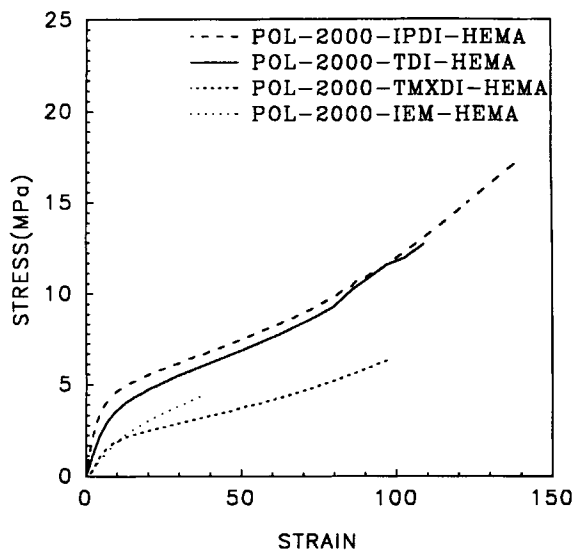


Figure 11 Effect of hard-segment type on the stress-strain curve.

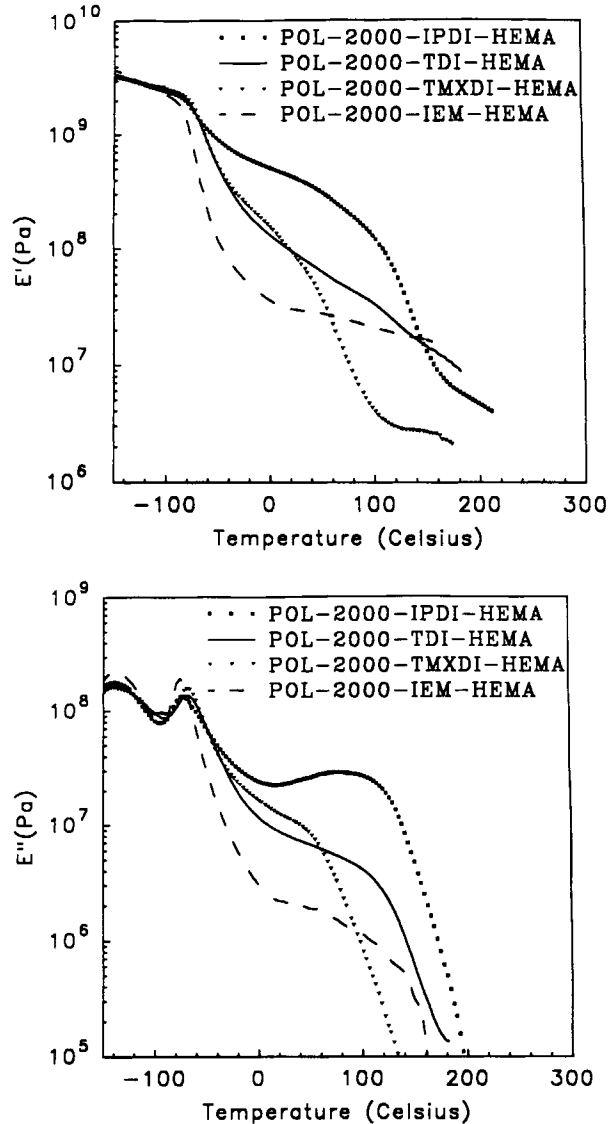


Figure 12 Effect of hard-segment type on DMTA spectra for PCL-2000-*x*-HEMA: (a) E' ; (b) E'' .

Effect of Soft-segment Molecular Weight and Crystallization on Cured Films

As noted in the Introduction, soft-segment molecular weight was studied extensively by Lin et al.¹² The results were confirmed in this study; the ultimate stress and modulus were higher for materials synthesized from the lower molecular weight oligomer. This resulted from a higher weight fraction of urethane acrylate material, which yields a higher cross-link density. A higher soft-segment molecular weight caused higher sample extensibility.

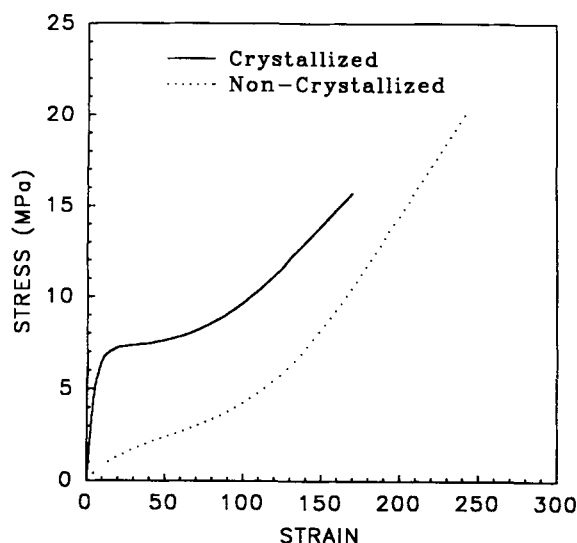
The soft-segment glass transition temperature dropped as the soft-segment molecular weight increased. The incremental T_g change resulting from a change in soft-segment molecular weight was

Table V Effect of Polyol Molecular Weight on Glass Transition Temperature

Material	Glass Transition Temperature (°C)
PPO-1000-IEM	-37
PPO-2000-IEM	-54
PPO-3000-IEM	-58
PPO-4000-IEM	-62

larger for the lower molecular weight materials. The change in T_g was 35°C when the molecular weight was changed from 650 to 2000 in POL and only 1°C when the molecular weight was changed from 2000 to 3000 in PCL. Data taken from Lin et al.¹² on poly(propylene oxide) (PPO)-IEM materials without diluent in Table V exhibit the same effect. The soft-segment phase may become purer at a faster rate when the molecular weight is changed in the former case. Also, the soft-segment endgroups that are immobilized in the hard-segment phase have an important role in the long-range cooperative motion that comprises the glass transition. Since these endgroups are a much larger percentage of the material synthesized with the lower molecular weight soft segment, the T_g behavior discussed above would result.

Even though samples were cross-linked, crystallization of the soft segment will change the mechanical properties considerably. Figure 13 shows two samples based on PCL-3000-IPDI-HEMA. Noticeable crystallization occurred during curing in the PCL-3000 materials at room temperature. The ul-


Figure 13 Effect of soft-segment crystallization on the stress-strain curve in PCL-3000-IPDI-HEMA.

timate elongation and stress at break were higher for the uncrystallized material, but the modulus is significantly higher for the crystallized material. The crystallites acted as physical cross-links, which increased the effective cross-link density. The toughness (area under the stress-strain curve) was approximately equal for the two materials.

PCL-3000 materials showed an endotherm in the DSC spectra at 50°C corresponding to melting of PCL crystallites. The melting temperature and heat of fusion is shown in Table VI. Except for the HEMA-40 material, a small amount of material crystallized in the nominally uncrystallized PCL-3000 materials in spite of efforts to prevent crystallization. Crystallization could have occurred after cross-linking as well. Material allowed to crystallize during curing had almost six times the percent crystallinity as that of the uncrystallized material based on heat of fusion data.

The heat-capacity change in the glass transition was significantly lower for the crystallized material since less soft segment participated in the glass transition. The T_g for the uncrystallized material was lower than that for the crystallized sample. The ends of the amorphous soft segment are subject to an immobilization effect caused by the crystals, an effect noticed in many crystallizable homopolymers. Also, crystallization could have occurred primarily with longer chains. The remaining amorphous shorter molecular weight chains would have a higher glass transition temperature.

DMTA spectra [Fig. 14(a) and (b)] show a substantial difference between the crystallized and uncrystallized materials. Between the soft-segment glass transition and melting, the storage modulus was much higher for the crystallized material, which agreed with the tensile data. At temperatures higher than 50°C, however, the modulus for the uncrystallized material was greater. Both samples failed at approximately 100°C; presumably, the data could

Table VI Heat of Fusion for PCL-3000 Samples

Material	Melting Temperature (°C)	Heat of Fusion (J/g)
PCL-3000-IPDI-HEMA CRYST	50	35.8
PCL-3000-IPDI-HEMA NONCRYST	45	6.31
PCL-3000-IPDI- HEMA-HEMA-20	47	5.48
PCL-3000-IPDI- HEMA-HEMA-40	—	—

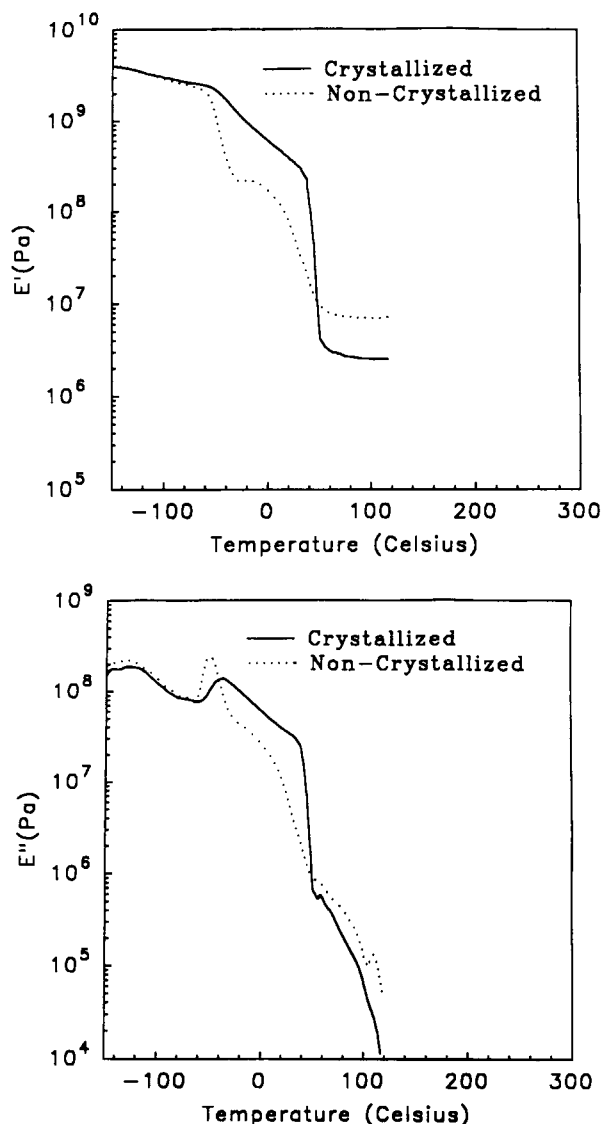


Figure 14 Effect of soft-segment crystallization on DMTA spectra for PCL-3000-IPDI-HEMA: (a) E' ; (b) E'' .

be extended out to much higher temperatures. Crystallization apparently inhibited cross-linking, probably by immobilizing acrylate groups. The peak in the loss modulus corresponding to the soft-segment glass transition occurred at higher temperatures and was not as intense for the crystallized material, which agreed with the DSC results. Crystallization also broadened this transition.

IV. CONCLUSIONS

Diluent level, hard-segment type, soft-segment molecular weight, and soft-segment crystallization were studied in UV-curable acrylates. The addition of

diluent increased the modulus and ultimate stress. The magnitude of the increase in modulus suggests that the rise was due to a combination of factors. The effect on ultimate strain depended on the hard-segment type. For PCL-2000 materials with HEMA diluent, the diluent did not change the ultimate elongation except at greater than 50 wt % diluent content, where the elongation fell rapidly. Materials with NVP diluent showed substantial necking and drawing at diluent contents of 40 wt %. In POL-2000-IPDI materials, ultimate elongation increased, whereas for POL-2000-TMXDI, ultimate elongation decreased as NVP diluent content increased. The hard-segment phase for the POL-TMXDI phase was very impure, and diluent increased the brittleness of this material because NVP was unable to preferentially migrate to the hard-segment phase. POL-IPDI materials were much better phase-separated; the NVP was able to exist almost solely in the hard-segment phase and toughen the material.

Previous studies suggest that hard-segment type does not affect mechanical properties of the material if the hard segment contains at least one six-membered carbon ring. However, TMXDI showed inferior properties compared to TDI or IPDI. IEM has been noted previously for producing UV-curable acrylates with low tensile properties, which was confirmed in this work. Soft-segment molecular weight also affected mechanical properties. These materials showed the importance of endgroup immobilization on the glass transition. Finally, allowing the soft segment to crystallize during curing changed mechanical properties dramatically. The modulus increased as crystallization increased, but the ultimate stress and ultimate elongation both decreased. Crystallization also inhibited cross-linking as evidenced by the lower plateau modulus in the crystallized sample above the melting point.

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