Synthesis, Characterization, and Structure of Glassy Diacetylene-Containing Segmented Block Copolyurethanes

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Received May 17, 1991; Revised Manuscript Received August 13, 1991

ABSTRACT: Diacetylene-containing segmented block copolyurethanes were prepared from 4,4'-diisocyanodiphenylmethane, 2,4-hexadiyne-1,6-diol, and a poly(propylene glycol) using a one-shot bulk polymerization process. Two copolymer series were produced: one containing different diacetylene contents and the second containing different amounts of a second short-chain diol, dipropylene glycol, but with approximately constant diacetylene content. The as-prepared, linear copolymer precursors were then thermally cross-polymerized via solid-state topochemical reactions within the diacetylene-containing phase, to yield insoluble and infusible materials. All the cross-polymerized copolymers were rigid at room temperature with glass transition temperatures ranging from 40 to 100 °C (DMTA). The effects of copolymer composition and the conditions for cross-polymerization on the morphology and properties of the materials were extensively studied using thermal and spectroscopic techniques. Transmission electron microscopy showed clearly the diacetylene-containing spherulites to be uniformly dispersed in the continuous, amorphous poly(ether-urethane) matrices. Significant phase mixing and disruption of the solid-state topochemical reactions in the copolymers resulted when the additional glycol DPG was introduced. Resonance Raman spectroscopy proved extremely useful for following the in situ formation of the polydiacetylene chains within the dispersed phase and for providing information concerning copolymer morphology.

Introduction

Following the original work by Wegner[1] on the solid-state topochemical polymerizations of diacetylene monomers, it has been shown[2-4] that similar reactions also occur in diacetylene groups in the repeat units of some linear polyurethanes, polyesters, and other polymers. It was generally concluded that the topochemical reaction, defined as cross-polymerization, caused cross-linking within the crystalline regions of a polymer, producing a network structure. In such cases, the substituent side groups are the polymer chains connecting the polydiacetylene backbones in the polymer networks. More recently, studies[5-7] on diacetylene-containing segmented copolymer elastomers have shown the potential of producing phase-separated materials with unique combinations of the optical and electrical properties of polydiacetylenes with the mechanical properties and processibility of linear polymers. Although a number of diacetylene-containing copolymers were synthesized, the processing and properties of the materials were far from optimized. Studies on copolyurethanes in particular were restricted to a limited range of model elastomers. Futhermore, most of the optical analysis of the elastomers was performed mainly to investigate color changes occurring during cross-polymerization or upon changes in the external environmental conditions. Typical examples are the study of thermo- and mechanochromism phenomena.[6,8]

The unusual optical properties of the polydiacetylene single crystals are related to the characteristics of their conjugated molecular backbones. For example, the single crystals produce intense resonance Raman scattering, and the stress-strain dependence of band positions in Raman spectra is of particular interest and has been extensively studied.[9-11] The Raman band positions have been found to shift substantially to lower frequencies when the polydiacetylene single crystals are subjected to tensile deformation along their molecular axes. This optomechanical phenomenon has enabled the molecular stress-strain behavior of single crystals to be evaluated spectroscopically by monitoring the Raman band positions. In fact, the technique has been used successfully to study the deformation micromechanics of other highly oriented polymers such as Kevlar[12] and gel-spun polyethylene fibers[13] and is being applied to a wide range of materials. The significance of using Raman spectroscopy as a microstress or microstrain probe in materials is becoming increasingly recognized.

The shifts in Raman band frequencies in a polymer during deformation are due to the changes in the bond lengths and bond angles, when the externally applied stress is transformed into the direct deformation of the covalent bonds. The Raman bands of polydiacetylene single crystals have been shown to be highly sensitive to deformation and the position of the triple bond stretching band, $\nu(C{\equiv}C)$, in particular, shifts by up to -20 cm^{-1}/% strain.[11] However, for less oriented and isotropic polymers, Raman spectral bands are generally insensitive to the overall strain in the bulk materials (shifts < 1 cm^{-1}/%)[14] since, rather than producing direct deformation in covalent bonds, most of the applied deformation causes other molecular deformation processes to occur. These include straightening and disentanglement of coiled chains, chain reptation, and viscous flow.

The main aim of this work was to produce alternative isotropic polymers with well-defined Raman spectra which are highly stress-strain sensitive. Rigid, glassy diacetylene-containing segmented block copolyurethanes have been prepared and the solid-state topochemical cross-polymerization of the diacetylene units carried out using thermal treatment. The structure, morphology, and thermal and optical properties were extensively studied using thermal and spectroscopical methods which included differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), dynamic mechanical thermal analysis (DMTA), wide-angle X-ray diffraction (WAXD), transmission electron microscopy (TEM), and Raman spectroscopy. The mechanical and optomechanical behavior and potential applications of the copolymers will be described elsewhere.[15]

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0024-9297/92/2225-0672$03.00/0

Table I
Chemical Structures and Properties of Reactants Used To Form Copolyurethanes

starting material	structure	equivalent weight, g/mol	T_m, °C	physical state
MDI	OCNRNCO[a]	125.13	40	solid
PPG	$[CH_2[OCH_2CH(CH_3)]_nOH]_2$	216.6		liquid
DPG[b]	$HO[CH_2CH(CH_3)O]_2H$	67.0	~95 (bp)	liquid
HDD	$HOCH_2C{\equiv}CC{\equiv}CCH_2OH$	55.0	112	solid

[a] R is the same as defined in Scheme I. [b] Mixture of isomers.

Table II
Percentage Weight Fractions, W, of Reactants Used in Formulations To Prepare Copolyurethanes of Various Hard-Segment Contents

copolymer code[a]	% W_{HDD}	% W_{PPG}	% W_{DPG}	% W_{MDI}	% HS[b]
P[0D0H]	0	63.4	0	36.6	0
P[0D5H]	3.7	55.7	0	40.6	12
P[0D10H	5.7	51.5	0	42.8	19
P[0D15H]	8.3	46.1	0	45.6	27
P[0D20H]	10.4	41.8	0	47.8	34
P[5D20H]	10.2	38.8	1.94	49.1	33
P[10D20H]	9.9	36.2	3.62	50.3	32
P[15D20H]	9.7	33.9	5.08	51.3	32

[a] In the general code P[xDyH], x and y signify DPG and HDD contents, respectively, in the copolymers. [b] Hard-segment content, HS, was calculated according to the equation $HS = W_{HDD}(1 + E_{MDI}/E_{HDD})$, where E_{MDI} and E_{HDD} are the equivalent weights of MDI and HDD, respectively.

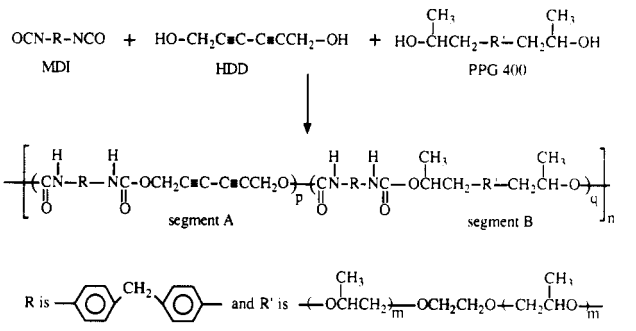
Experimental Section

A. Synthesis of Diacetylene-Containing Segmented Copolyurethanes. a. Starting Materials. 4,4'-Diisocyanodiphenylmethane, MDI (BDH), was purified by hot filtering through a 3A sintered-glass funnel. Poly(propylene glycol), PPG-400 (Fluka), was dehydrated under vacuum (0.01 mmHg) in a rotary-film evaporator at 80 °C for 16 h. Dipropylene glycol, DPG (Fluka), was vacuum distilled over 4A molecular sieves. 2,4-Hexadiyne-1,6-diol, HDD, was synthesized from propargyl alcohol (Fluka) using the procedure described by Hay.[16] HDD was freshly recrystallized from ethyl acetate and vacuum dried for 5 h prior to use. The equivalent weights (molecular weight per functional group) of all the starting materials were determined by end-group analysis and the results are summarized in Table I.

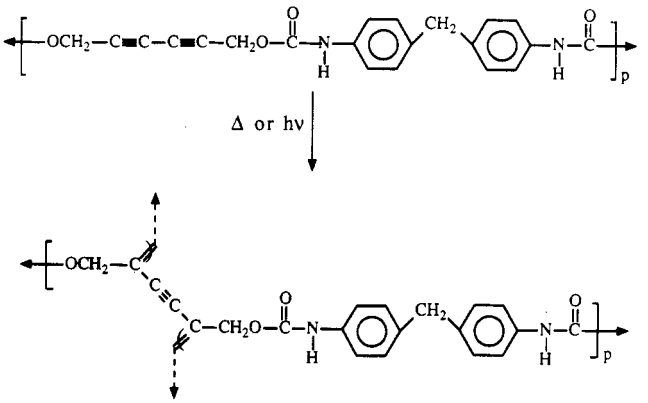
b. Synthesis of the As-Prepared Linear Diacetylene-Containing Segmented Block Copolymers via One-Shot Bulk Polymerization. Two series of diacetylene-containing copolymers with various compositions were prepared following the same procedure, and in both series, stoichiometric equivalence of NCO and total OH groups was maintained. The compositions of these copolymers are summarized in Table II. The synthetic procedure used can be described as follows. The required amounts of PPG-400, and DPG in some cases, were weighed directly into a round-bottom flask with a detachable four-neck top. The required weight of freshly recrystallized HDD was added to the flask before it was immersed in a water bath at 80 °C. The reactants were stirred under nitrogen purge until the HDD was dissolved in the polyether diol and the mixture became clear. The required amount of premelted MDI (45 °C) was then poured into the reaction flask, which was immediately transferred to a cold-water bath to avoid an excessive exotherm. The reaction mixture was stirred for 2 h at 60 °C and then cast into a preheated, picture-frame mold and cured for another 2 h at 60 °C. The product was a colorless, soluble, transparent or translucent copolymer sheet. The as-prepared samples were refrigerated in the dark to prevent cross-polymerization from occurring by exposure to room light. The polymerization process and the structures of the poly(ether–urethane) segments and the diacetylene-containing hard segments are illustrated in Scheme I. However, the structures of copolymers formed using two chain extenders, namely HDD and DPG, are more complex.

c. Solid-State Topochemical Cross-Polymerization of the As-Prepared Copolymer Precursors. Linear segmented diacetylene-containing copolymers can undergo solid-state cross-polymerization by irradiation or thermal annealing to produce deeply colored, insoluble and infusible materials with a cross-linked network structure. In this work, cross-polymerized copolymers were prepared from the as-prepared copolymer precursors by thermal treatment at 100 °C for 40 h unless otherwise stated. The cross-polymerization reaction occurs in the diacetylene-containing hard segments and is illustrated in Scheme II, which indicates the formation of the polydiacetylene chains.

Scheme I



Scheme II



A more detailed picture of the hard-segment cross-polymerization is given in Figure 1, which shows the idealized structures of the urethane–diacetylene hard segments (MDI/HDD) before and after cross-polymerization. The formation of a three-dimensional polyurethane–diacetylene network is clearly illustrated in the structure after cross-polymerization.

The effects of thermal treatment conditions upon the material properties were analyzed using thermal and spectroscopic methods and will be discussed in detail later. Dramatic color changes were also observed in the diacetylene-containing copolymers during the cross-polymerization process. For example, copolymer P[0D20H] changes from yellowish-white to grey to blue to dark purple with increasing extent of thermal treatment.

B. Characterization of the Copolymers. a. Molar Mass Determination for the As-Prepared Copolymers. All the as-prepared copolymers were soluble in THF, thus enabling average molar masses and the molar mass distribution of each sample to be determined by gel-permeation chromatography (GPC). A Waters Millipore 510 high-pressure liquid chromatograph (HPLC) was used, which was equipped with three columns (Polymer Laboratories) packed with P-gel (cross-linked polystyrene–divinyl benzene with particle size of 10 μm and porosities of 50, 10^3, and 10^5 nm, respectively). The eluent was THF and the flow rate was kept at 1.0 mL/min. A Knauer differential refractometer was used to detect the polymer fractions and the temperature was controlled at 30 °C. The system was calibrated using polystyrene standards of known molar masses. Table III

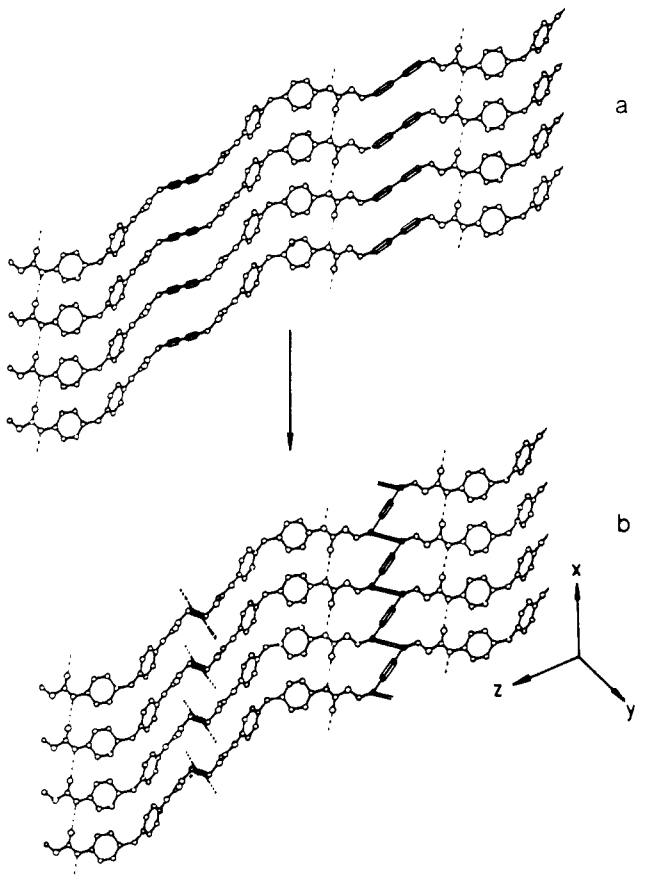


Figure 1. Schematic representation of the topochemical solid-state cross-polymerization within diacetylene-containing hard-segment domains. The idealized structure of the MDI/HDD hard segment are shown (a) before and (b) after the cross-polymerization. The direction of polyurethane chains is along the z axis, and the directions of polydiacetylene chains are along the x and y axes. Carbon atoms in both the conjugated diacetylene monomer units and the polydiacetylene backbones are represented by the filled circles.

Table III
Average Molar Masses and Polydispersities of the As-Prepared Diacetylene-Containing Copolymers

copolymers	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
P[0D0H]	8600	17310	2.00
P[0D5H]	12040	27021	2.25
P[0D10H]	9610	23250	2.42
P[0D15H]	11620	25500	2.19
P[0D20H]	8625	18826	2.18
P[5D20H]	9320	21716	2.33
P[10D20H]	10420	21470	2.06
P[15D20H]	8762	21120	2.41

lists the average molar masses and the polydispersities of the as-prepared copolymers. It should be noted that the average molar masses of the samples are all in the range of 8000–12000 g/mol and the polydispersities are in the range of 2.00–2.50, which is typical for polyurethanes. These data suggest that any differences in the properties of these materials are not due to variations in molar mass or molar mass distribution. However, owing to the nature of the GPC technique, the molar mass data listed in Table III are more useful for comparative purposes rather than as absolute molar mass values.

b. Thermal Analysis. Differential scanning calorimetry (DSC) and dynamic mechanical thermal analysis (DMTA) were carried out using a Du Pont 990 thermal analyzer and a Polymer Laboratories' DMTA analyzer, respectively. In DSC analysis, samples of about 10 mg were used and the scans were performed in air between −100 and 300 °C using a heating rate of 20 °C/min. DMTA analysis was performed at 1 Hz over the temperature range of −100 to 250 °C at a heating rate of 5 °C/min. Rectangular specimens (50 × 10 × 2.5 mm³) were used in the dual-cantilever mode. Thermogravimetric analysis was carried out using a Stanton Redcroft thermobalance. Samples of 10 mg were weighed accurately into a clean platinum crucible and tested under nitrogen atmosphere from room temperature to 800 °C at a heating rate of 3 °C/min.

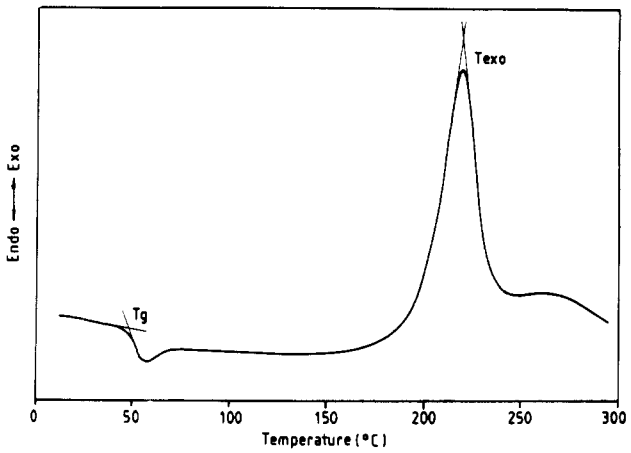


Figure 2. DSC curve for as-prepared, linear copolyurethane P[0D15H] containing 27% weight fraction of diacetylene–urethane hard segment.

c. Raman Spectroscopy. Raman spectra were obtained using a 10-mW 632.8 nm He/Ne laser (1 mW on the samples). A modified Nikon optical microscope with x40 objective of 0.65 numerical aperture was used to focus the incident laser beam to a 2-μm spot on the specimens. The 180° back-scattered light was collected by the objective lens and analyzed by a Spex 1403, 0.85-m double monochromator with 1800 grooves/cm gratings. A Wright Instruments charge-coupled device (CCD) (liquid nitrogen cooled) was employed to detect the Raman scattering with a 0.1 cm^{-1} resolution. The CCD camera is a highly sensitive, low-noise detector. In this work, a scanning time of 10 s was typical for a spectral window of 40 cm^{-1}.

d. Wide-Angle X-ray Diffraction (WAXD). The X-ray diffraction patterns were recorded with a Philips PW 1710 horizontal wide-angle X-ray diffractometer, operating at 10 kV and using CuKα radiation with a nickel filter.

e. Transmission Electron Microscopy (TEM). Ultrathin (<100 nm) sections of the copolymers obtained using a Reichert-Jung ultramicrotome were examined using a Philips 301 transmission electron microscope operated at 100 kV. All samples were thermally treated at 100 °C for 40 h before sectioning.

Results and Discussion

A. Cross-Polymerization of As-Prepared Copolymer. The conditions of cross-polymerization, that is the temperature and time used to thermally treat the as-prepared copolyurethanes, are critical in determining the subsequent thermal, mechanical, and spectroscopic properties of the materials. Preliminary experiments were carried out to determine cross-polymerization conditions, and their effects on subsequent thermal properties of the copolymers were monitored by DSC. The DSC curves for all the copolyurethanes showed essentially two main thermal transitions between 0 and 300 °C. For example, Figure 2 shows the DSC trace of as-prepared, linear P[0D15H]. The lower temperature transition, observed as an endothermic base-line shift, is associated with the main glass transition of the matrix occurring at T_g. The much more intense, higher temperature exothermic peak located at T_{exo} is almost certainly due to the reaction exotherm of the diacetylene cross-polymerization reactions, although some thermal degradation, inevitable under the DSC testing conditions used, may also be occurring. Subsidiary thermogravimetric analysis experiments were therefore carried out to quantify the extent of thermal degradation occurring in the copolyurethanes. The data shown in Figure 3 are typical, with degradation commencing at around 200 °C. In air, the degradation appears

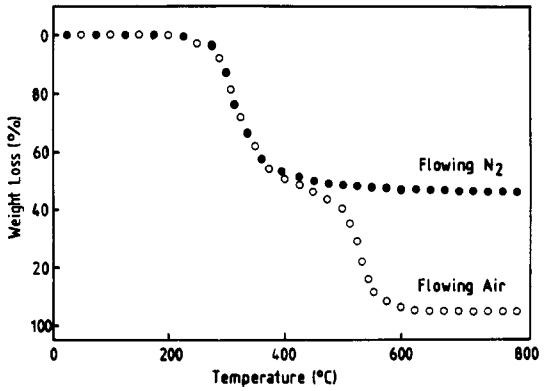


Figure 3. TGA traces of thermally treated (100 °C/40 h) copolymer P[0D20H] containing 34% weight fraction of diacetylene–urethane hard segment.

Table IV
Effects of Copolymer Composition on the Temperatures for 1% Weight Loss ($T_{1\%}$) in Air for Copolymers Cross-Polymerized at 100 °C/40 h

copolymers	% W_{HDD}	% W_{DPG}	% HS	$T_{1\%}$, °C
P[0D0H]	0	0	0	170
P[0D5H]	3.7	0	12	180
P[0D10H]	5.7	0	19	192
P[0D15H]	8.3	0	27	205
P[0D20H]	10.4	0	34	217
P[5D20H]	10.2	1.94	33	216
P[10D20H]	9.9	3.62	32	220
P[15D20H]	9.7	5.08	32	212

to occur in two stages and is essentially complete at about 600 °C, whereas in nitrogen, degradation occurs in a single stage between 200 and 400 °C with a ~50% weight loss, producing a relatively stable char. Further degradation in nitrogen thus proceeds at a much slower rate and the weight loss is still less than 60% even at 800 °C. It is interesting to note that degradation in this diacetylene-containing copolymer is initiated at approximately the same temperature (~200 °C in Figure 3), irrespective of whether air or nitrogen is used, since degradation in air might be expected to commence at a lower temperature.

The temperature at which a 1% weight loss in air was observed was defined as the onset temperature for degradation, designated $T_{1\%}$. Values of $T_{1\%}$, reported in Table IV, show a steady increase from 170 to 217 °C as hard-segment content increases from 0 to 34%, whereas $T_{1\%}$ remains essentially constant (212–220 °C) as the DPG content increased at constant hard-segment content. These data suggest, therefore, that thermal stability is improved by increasing the diacetylene content of the copolymers. The enhanced thermal stability is attributed to the increasing degree of cross-linking and the inherently higher stability of the polydiacetylene chains, as the diacetylene content increases. Thermal degradation in a variety of polydiacetylenes has been shown[17] to result mainly from reactions associated with the side groups rather than with the polydiacetylene backbone. Since polyurethanes are known to have relatively poor thermal stabilities, it may be concluded that degradation in the present copolymers occurs mainly by degradation reactions involving the poly(ether–urethane) groups. This proposal is supported by previous work on the degradation of polydiacetylenes:[17] derivatives with urethane-containing side groups show very similar weight-loss behavior to that observed in this study, and the weight losses during TGA indicate that the urethane group dissociates in the temperature range 200–400 °C. This implies that the thermal stability of the copolymers is mainly controlled by the properties of side groups. Copolymers with enhanced thermal stability may be obtained by using more stable

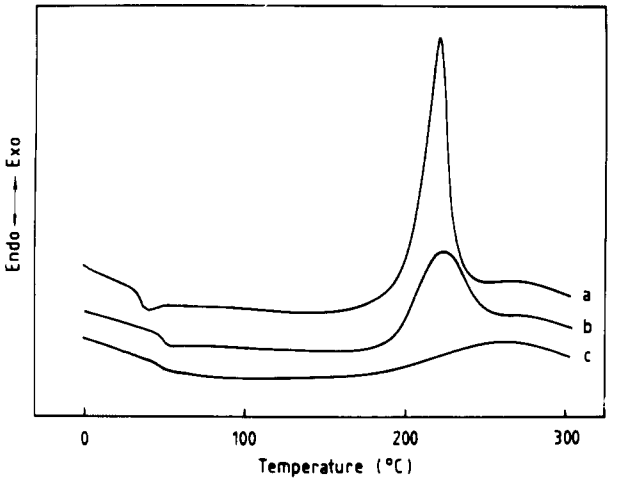


Figure 4. DSC curves of copolymer P[0D15H] showing the effects on transitional behavior of cross-polymerization temperature used during thermal treatment for 20 h: (a) as-prepared, (b) 100 °C, (c) 160 °C.

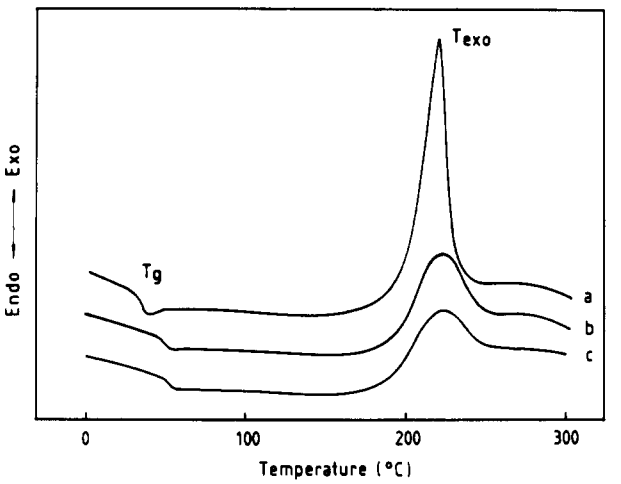


Figure 5. DSC curves of copolymer P[0D15H] showing the effects on transitional behavior of cross-polymerization time used for thermal treatment at 100 °C: (a) as-prepared, (b) 20 h, (c) 40 h.

side groups such as polyamide and polyimide. The data in Table IV therefore suggest that there is some contribution from thermal degradation to the overall intensive exothermic transition occurring between 150 and 250 °C (see Figure 2), although the cross-polymerization of diacetylene-containing hard segments is mainly responsible for the very intense exothermic peak at T_{exo}.

Further studies were carried out to establish the optimum conditions for efficient cross-polymerization with minimum thermal degradation. Copolymers were thermally treated for 20 h at 100 and 160 °C, and their DSC behavior was compared to that of as-prepared samples. Figure 4 shows comparative DSC traces for P[0D15H]. Thermal treatment at 100 °C causes an increase in T_g from 29 to 41 °C and a large decrease in intensity of the exothermic peak at ~220 °C. However, after heating at 160 °C, the transition at T_g (38 °C) is much less intense and broadened, and the exothermic peak has virtually disappeared. Both observations indicate that some degradation has occurred during thermal treatment. Figure 5 shows comparative DSC traces for P[0D15H] which has been subjected to thermal treatment at 100 °C for 20 and 40 h. Increasing the time resulted in a small change in degree of cross-polymerization (without additional degradation), but longer thermal treatment at 100 °C had little effect. The data in Figures 4 and 5 show that complete cross-polymerization, as indicated by the com-

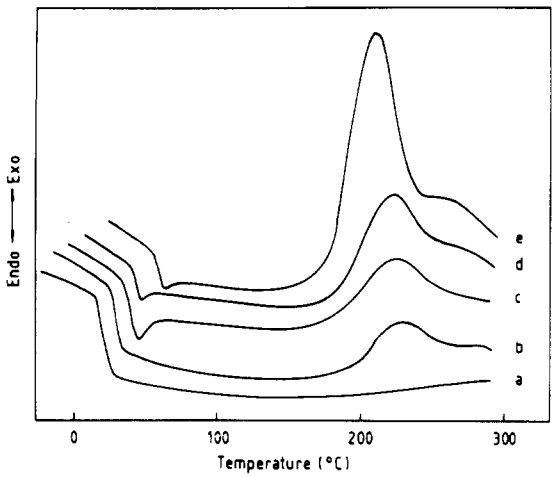


Figure 6. DSC curves of thermally treated (100 °C/40 h) copolyurethanes containing different percentage weight fractions of diacetylene–urethane hard segment: (a) 0% (P[0D0H]), (b) 12% (P[0D5H]), (c) 19% (P[0D10H]), (d) 27% (P[0D15H]), (e) 34% (P[0D20H]).

plete absence of the exothermic peak, cannot be achieved without causing degradation. Conditions of 100 °C for 40 h were considered optimum and all copolymers were thermally treated accordingly.

B. Differential Scanning Calorimetry (DSC). The presence of polydiacetylene chains has a significant effect on the thermal properties of the copolyurethanes. Figure 6 shows DSC curves for thermally treated (100 °C/40 h) copolymers formed using increasing amounts of HDD. The matrix, P[0D0H] (curve a), shows only a glass transition (17 °C), and increasing the HDD content causes the glass transition to decrease in intensity and shift to higher temperatures, which is consistent with increased phase mixing between the poly(ether–urethane) matrix and dispersed diacetylene-containing phases as the hard-segment content increases.[18] More significant is the increase in intensity of the cross-polymerization exotherm, which also shifts to lower temperatures, as the HDD content increases. The DSC results derived from the curves in Figure 6 are compared with those of as-prepared copolymers in Table V and show that thermal treatment shifts both T_g and T_{exo} to higher temperatures for all the copolymers studied. The shift in T_g increases with hard-segment content and is much greater than the shift in T_{exo}, which again confirms the increasing degree of phase mixing.

Dipropylene glycol (DPG) was incorporated into formulations for some of the copolymers in order to raise the glass-transition temperature and to increase the intrinsic stiffness of the poly(ether–urethane) phase, without significant alternation of the diacetylene-containing hard-segment content. The effects of DPG on the DSC transitional behavior of the copolymers are shown in Figure 7. The incorporation of only ~5% by weight of DPG is sufficient to increase the T_g by 17 °C, despite the very small reduction in hard-segment content, although the intensity of the glass transition is reduced. However, the effects on the cross-polymerization exotherm are much more significant with a small upward trend in T_{exo} accompanied by a large decrease in peak intensity. Similar trends were observed for as-prepared copolyurethanes, and thermal treatment, as before, shifted T_g and T_{exo} to higher temperatures but by amounts (~14 and ~5 °C, respectively) which do not vary significantly with DPG content.

The reduced exothermic activity implies that although the hard-segment content is essentially constant, the number of diacetylene units capable of undergoing solid-state topochemical cross-polymerization reactions is reduced as DPG content in the copolymers increases. Clearly the presence of DPG during copolyurethane preparation does not favor the aggregation of the diacetylene-containing oligomers and disrupts the formation of hard-segment domains. This in turn indicates increased phase-mixing between poly(ether–urethane) and polydiacetylene-containing phases as DPG content increases, which is consistent with the observed changes in the DSC transitional behavior occurring at T_g and T_{exo}. The effects of DPG content on the morphology and optical properties of the copolymers are discussed further in later sections on dynamic mechanical thermal and spectroscopic analyses, and the effect on mechanical properties will be described in a following paper.[15] Similar effects of the variation in hard-segment structural order on properties have also been reported[7] for diacetylene-containing copolyester elastomers formed with or without a second chain extender: copolyesters formed using an additional chain extender showed reduced photoreactivity.

C. Dynamic Mechanical Thermal Analysis (DMTA). DMTA, compared to DSC, provides a more complete characterization of the temperature-dependent properties of phase-separated copolymers, in which variations in transitions and modulus can be monitored in relation to changes in structure and morphology. This is particularly relevant in the present copolyurethanes in which cross-linking reactions occur during the course of a DMTA experiment. For example, the DMTA curves in Figure 8 for as-prepared P[0D20H] show several interesting features. The tan δ–temperature (tan δ/T) curve shows three distinctive peaks at increasing temperatures designated T_{SEC}, T_g, and T_{HS}. The peak at T_{SEC} (~−60 °C) is due to local relaxations involving oxypropylene units in the polyether phase, and there is a corresponding inflection in the glassy region of the modulus–temperature (log E'/T) curve. The most intense peak is ascribed to the main glass transition at T_g (~50 °C) and the associated decrease in log E' (10^9–10^7 Pa) is consistent with the short PPG-400/MDI repeat structure of the poly(ether–urethane) phase which forms the major proportion of the copolymer. Despite the as-prepared P[0D20H] being linear, there is a pseudorubbery plateau between ~80 and 110 °C attributable to the presence of a high concentration of hydrogen-bonded aromatic urethane groups in the poly(ether–urethane) phase and the more ordered diacetylene-containing hard-segment domains, which act as macroscopic cross-links. As the temperature increases above 100 °C, hydrogen bonds begin to dissociate and the hard segments undergo an order–disorder transition, and as they soften, log E' decreases and tan δ increases. However, as the temperature continues to rise, the rate of cross-polymerization in the hard segments rises rapidly and the high degree of localized covalent cross-linking prevents further structural disruption. Consequently, log E' increases rapidly (from 10^6 to 10^7 Pa) and tan δ decreases sharply. The peak at T_{HS} (~130 °C) arises, therefore, from the combination of opposing relaxations, namely, reversible structural disordering and irreversible cross-linking. The final level of modulus (and the minimum in tan δ) is determined by the efficiency of cross-polymerization achieved within the imperfect hard-segment domains, and by the onset of thermal degradation as the temperature exceeds 200 °C, which causes log E' to decrease and tan δ to increase.

Considering the symmetric structure of the hard-segment repeat unit and the low molar mass of hard segment chains, the hard-segment domains in the linear, as-prepared copolymers might be expected to show some crystallinity. However, no endothermic behavior associ-

Table V
Effect of HDD Content upon the Thermal Properties (DSC) of As-Prepared and Thermally Treated (100 °C/40 h) Copolyurethanes

samples	% W_{HDD}	% HS	as-prepared		cross-polymerized	
			T_g, °C	T_{exo}, °C	T_g, °C	T_{exo}, °C
P[0D0H]	0	0	16		17	
P[0D5H]	3.7	12	20	240	26	245
P[0D10H]	5.7	19	25	226	34	230
P[0D15H]	8.3	27	29	218	42	225
P[0D20H]	10.4	34	35	209	51	216

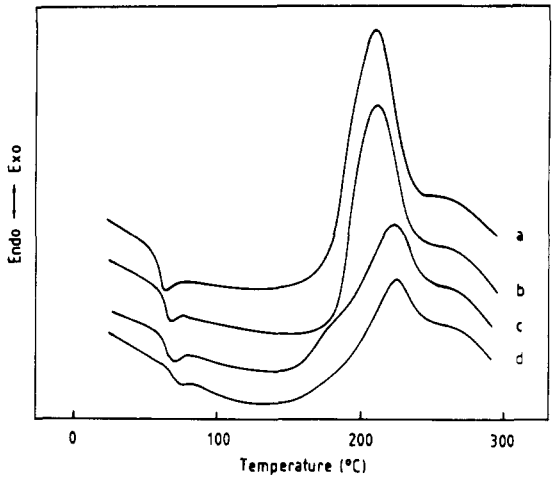


Figure 7. DSC curves of copolymers formed using different amounts (% by weight) of DPG. Samples contain ~33% by weight of diacetylene–urethane hard segment and were thermally treated at 100 °C for 40 h: (a) 0% (P[0D20H]), (b) 1.94% (P[5D20H]), (c) 3.62% (P[10D20H]), (d) 5.08% (P[15D20H]).

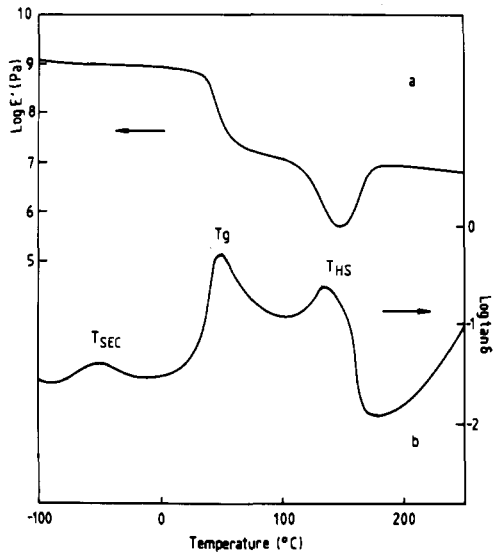


Figure 8. DMTA curves of as-prepared, linear copolyurethane P[0D20H] containing 34% weight fraction of diacetylene–urethane hard segment: (a) flexural storage modulus, E'; (b) loss tangent, tan δ.

ated with hard-segment melting or order–disorder transition was observed between ~50 and 150 °C in DSC curves (see Figure 6). This may be due to the low hard-segment content and paracrystalline nature of the hard-segment domains. These transitions, therefore, involve relatively small energy changes and it is possible that they were not detectable during DSC experiments. However, it is also probable that these weak endothermic processes are masked completely by the much more intense and extensive exothermic transition arising from the cross-polymerization of diacetylene units.

The presence and relative locations and intensities of the transitions vary significantly with copolymer compo-

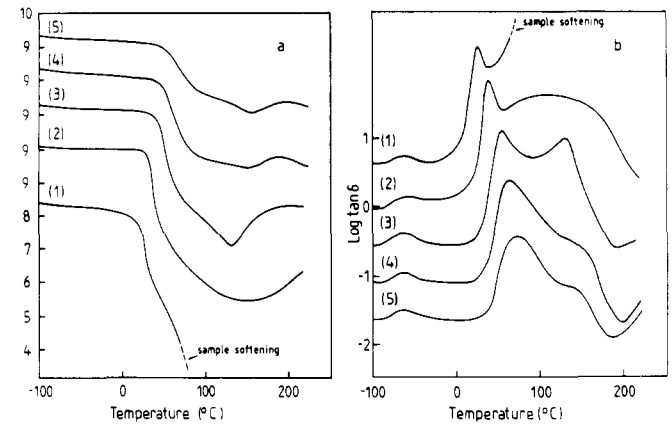


Figure 9. DMTA curves of thermally treated (100 °C/40 h) copolymers showing the effects of increasing weight fraction of diacetylene–urethane hard segment on (a) flexural storage modulus, E', and (b) loss tangent, tan δ: (1) 0% (P[0D0H]), (2) 12% (P[0D5H]), (3) 19% (P[0D10H]), (4) 27% (P[0D15H]), (5) 34% (P[0D20H]). The full-scale on the left-hand ordinate in the log E'/temperature diagram is for curve 1 and the full-scale on the left-hand ordinate in the tan δ/temperature diagram is for curve 5.

sition and thermal treatment conditions. The effects of increasing hard segment contents on DMTA behavior are shown in Figure 9,[30] and derived peak temperatures and intensities are summarized in Table VI. The polyurethane P[0D0H] is an amorphous, linear material and shows only secondary and glass transitions before softening completely at about 90 °C prior to becoming liquid. The presence of cross-linked poly(diacetylene–urethane) hard segments transforms the DMTA curves, although the secondary peak at T_{SEC} (~–65 °C) is essentially unaffected. The glass transition shifts to higher temperatures and broadens as hard-segment content increases, again confirming that increased phase mixing has occurred. Also evident is the development of the pseudorubbery plateau in log E'/T curves at around 100 °C. At low hard-segment contents, the hard-domain structure is not very well-defined and the extent of cross-polymerization achieved during thermal treatment appears to be low. Consequently the peak intensities and the increases in log E' occurring around T_{HS} during DMTA testing are significant. In contrast, for the higher hard-segment-content materials (curves 4 and 5 in Figure 9), the intensities of the tan δ peaks and the increases in log E' are much smaller, and occur at higher temperatures, indicating that much smaller proportions of residual diacetylene units, present after thermal treatment, undergo further cross-polymerization during DMTA analysis.

The effects of DPG content on DMTA behavior are evident from the curves in Figure 10. As before, the secondary relaxation at –65 °C is unaffected. However, the gradual elimination of the high temperature shoulder at T_{HS} is tan δ/T curves is clear evidence of the disruption of diacetylene-containing hard-segment domains caused by the incorporation of increasing amounts of DPG during copolymer formation. As a result, phase mixing increases

Table VI
Effects of HDD or Hard-Segment Content on the Transitional Behavior (DMTA) of Thermally Treated (100 °C/40 h) Copolymers

copolymer	% W_{HDD}	% HS	T_g, °C	tan δ	T_{HS}, °C	tan δ	T_{SEC}, °C	tan δ
P[0D0H]	0	0	25 (17)[a]	1.64			−65	0.04
P[0D5H]	3.7	12	40 (26)	1.58	140	1.12	−65	0.04
P[0D10H]	5.7	19	55 (34)	0.98	130	0.72	−65	0.03
P[0D15H]	8.3	27	65 (42)	0.60	150	0.07	−65	0.03
P[0D20H]	10.4	34	73 (51)	0.41	145	0.06	−65	0.03

[a] Values in parentheses are obtained from DSC.

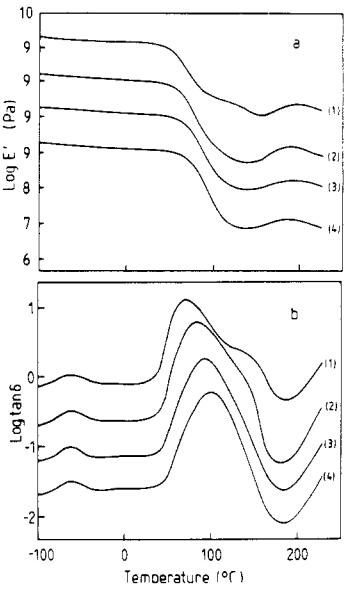


Figure 10. DMTA curves of copolyurethanes showing the effects on (a) flexural storage modulus, E', and (b) loss tangent, tan δ, of incorporating increasing amounts (% by weight) of DPG. Samples contain ~33% by weight of diacetylene–urethane hard segment and were thermally treated at 100 °C for 40: (1) 0% (P[0D20H]), (2) 1.94% (P[5D20H]), (3) 3.62% (P[10D20H]), (4) 5.08% (P[15D20H]). The full-scales on the left-hand ordinate are for sample 4.

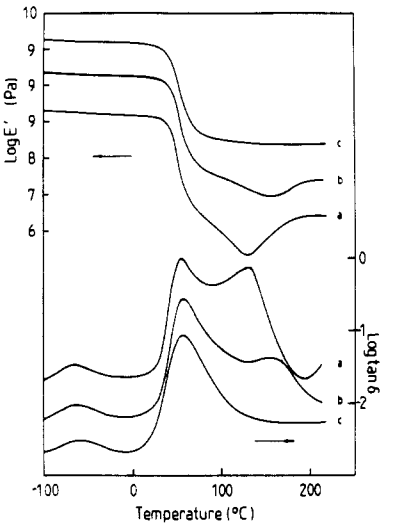


Figure 11. DMTA curves of copolymer P[0D10H] showing the effects on E' and tan δ of the cross-polymerization temperature used during thermal treatment for 40 h: (a) 100 °C, (b) 140 °C, (c) 160 °C. The full-scales are for the curves of sample a.

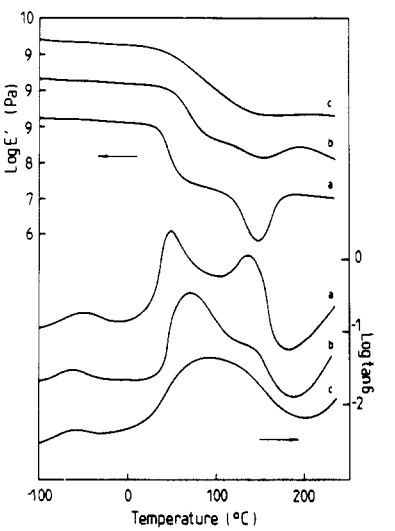


Figure 12. DMTA curves of copolymer P[0D20H] showing the effects on E' and tan δ of increased cross-polymerization temperature used during thermal treatment for 40 h: (a) as-prepared, (b) 100 °C, (c) 160 °C. The full-scales are for the curves of sample b.

as evidenced by the broadening of the glass transition and the upward shift in T_g by up to 25 °C as DPG content is increased to only about 5% by weight. It should be noted that the T_g values obtained from DMTA are significantly higher than those from DSC. Such discrepancies were found before[19] and can be attributed to experimental differences between these two techniques, and to the definition of T_g values as the onset temperatures in DSC and peak temperatures in DMTA.

Thermal treatment has significant effects on the DMTA behavior as shown by the curves in Figures 11 and 12 for copolymers containing 19 and 34% hard segments, respectively. Increasing the cross-polymerization temperature to 160 °C has little effect on the secondary transition (−65 °C) or, in the case of P[0D10H], on the glass transition (~58 °C). However, for P[0D20H], there is a pronounced reduction in intensity and a 40 °C increase in T_g. The extent of hard segment cross-polymerization should increase with the temperature used in thermal treatment, which might explain the decrease in peak intensity and the upward shift in T_{HS} for the residual diacetylene units capable of further cross-linking during the DMTA experiment. However, the temperatures 140 and 160 °C used exceed the hard-segment order–disorder transition ($T_{HS} \approx 130$ °C, see Figure 8) for as-prepared materials so that true solid-state topochemical cross-polymerization is not being achieved under these conditions. The order–disorder transition occurs over the temperature range 110–150 °C, so that at 140 °C the hard domains are partially disrupted whereas, at 160 °C, there is complete disruption. In the latter case, the copolyurethane is phase mixed and cross-polymerization occurs within uniformly dispersed hard segments comprising very few closely associated diacetylene units. Also the occurrence of thermal degradation at 160 °C cannot be ignored. The much more significant shift in T_g and broadening of the glass transition for P[0D20H] in Figure 12 is a direct result of the higher hard-segment content, that is, the higher concentration of diacetylene units.

D. Raman Spectroscopy. It was found[5,20] that certain cross-polymerized diacetylene-containing copolymers share strikingly similar Raman spectra with their polydiacet-

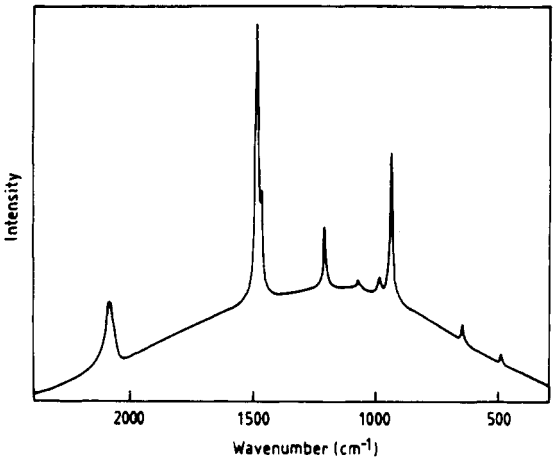


Figure 13. The resonance Raman spectrum of cross-polymerized (100 °C/40 h) copolymer P[5D20H].

ylene single-crystal analogues. A strong dependence of the optical properties upon sample structure and morphology has been demonstrated in some diacetylene-containing elastomers from studies of the photoreactivity and the thermochromism effect using UV/visible absorption spectroscopy.[6] In fact, the unique optical properties are the result of the conjugated polydiacetylene chains formed through the topochemical solid-state cross-polymerization of the diacetylene monomer units within the somewhat ordered hard segments. This in turn is mainly controlled by the structure and morphology of the copolymers as well as the conditions for the cross-polymerization. In this work, resonance Raman spectroscopy (RRS) was employed to examine the optical properties of the copolymers and to monitor the formation of the polydiacetylene chains in the hard segments.

The Raman spectrum of the cross-polymerized copolymer P[5D20H], obtained using a 632.8-nm He-Ne laser, is shown in Figure 13, and a similar well-defined spectrum was also observed in copolymer P[0D20H]. Four major Raman scattering bands were detected at 2090, 1480, 1205, and 940 cm^{-1}, and they can be assigned as the C≡C triple bond stretching mode, ν(C≡C), the C=C double bond stretching mode, ν(C=C), the C—C=C bending mode, δ(C—C=C), and the C—C≡C bending mode, δ(C—C≡C), respectively. Other small peaks observed in these spectra may be due to coupling of vibrations between the polydiacetylene backbone and the side groups.[21] It is the selectivity of the resonance enhancement that makes the Raman signals from the urethane moieties of the copolymers less prominent. Thus the Raman spectra obtained are almost free of interference caused by the scattering from the polyurethane segments. However, well-defined Raman spectra have not been obtained using 488 or 514.7-nm Ar ion laser. The Raman signals of polydiacetylene chains were completely lost in the intense fluorescence background. Indeed, the resonance effect is essential to guarantee a well-defined Raman spectra in this case. It should be emphasized that one of the objectives of the work was to develop new materials which combine the controllable mechanical properties and the processibility of polyurethanes with the unique optical properties of polydiacetylenes. Of particular interest was the development of materials having resonance Raman spectra with specific stress or strain sensitivity, for possible applications as optical stress or strains sensors. The use of Raman spectroscopy, therefore, is vital in determining which copolymer compositions and thermal treatment conditions (to achieve efficient cross-polymerization) provide materials suitable for such applications. Furthermore, characterization by Raman spectroscopy should provide additional information about the morphological structure of the copolymers.

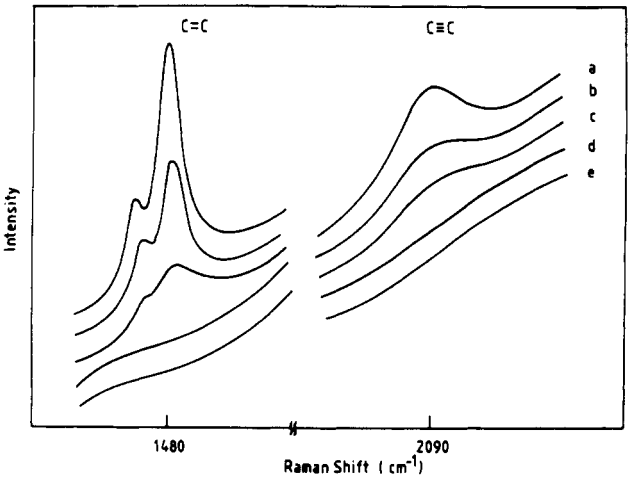


Figure 14. Variations in Raman bands associated with C=C and C≡C stretching modes at 1480 and 2090 cm^{-1}, respectively, in the spectra of thermally treated (100 °C/40 h) copolymers containing different weight percentages of diacetylene–urethane hard segments: (a) 34% (P[0D20H]), (b) 27% (P[0D15H]), (c) 19% (P[0D10H]), (d) 12% (P[0D5H]), (e) 0% (P[0D0H]). Curves are shifted vertically for clarity.

Unlike infrared absorption, which increases with the sample thickness, the intensity of Raman scattering is linearly related to the concentration of the scattering species, almost regardless of the sample thickness. In this case, the intensity depends upon the concentration of the polydiacetylene chains formed in the hard-segment domains. Raman spectroscopy was adopted to monitor the formation of the polydiacetylene chains and to study the factors which control the degree of the cross-polymerization, such as the copolymer coposition, morphology, and conditions of thermal treatment. In the present work, the intensity changes in the Raman spectra were monitored using the C=C double bond stretching mode band and the C≡C triple bond stretching mode band at about 1480 and 2090 cm^{-1}, respectively, instead of using the whole spectrum. Efforts were made to correlate the results from Raman spectroscopy with those from other techniques such as thermal analysis.

Figure 14 illustrates the Raman peaks of the C=C double bond and the C≡C triple bond stretching mode obtained from the copolymers with various diacetylene (HDD) contents which were cross-polymerized under identical conditions (100 °C/40 h). Steady increases of the intensities of both bands are clearly observed with increasing HDD content which correspond to the increase in the concentration of the polydiacetylene chains in the copolymers after the cross-polymerization. However, Figure 15 shows clearly that the intensities of the Raman bands of the C=C double bond and the C≡C triple bond stretching mode diminish with increasing DPG content in the copolymers which have approximately constant hard-segment content. Eventually, the Raman signals of the polydiacetylene species can no longer be detected in copolymer P[15D20H] containing 5.08% by weight DPG. This provides further evidence that the inclusion of DPG causes significant changes in the morphology of these copolymers. Thermal and dynamic mechanical thermal analysis revealed that the inclusion of DPG, however small the amount, gave rise to severe phase mixing of the copolymers and possibly disrupted the crystallization and ordering of the hard segments. Since ordering of the diacetylene-containing hard segments is crucial if solid-state topochemical cross-polymerization is to occur, then obviously the presence of DPG is directly responsible for the

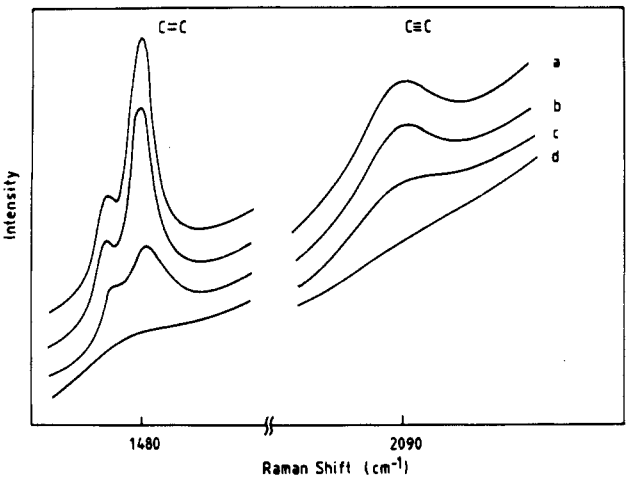


Figure 15. Variations in Raman bands associated with C=C and C≡C stretching modes at 1480 and 2090 cm^{-1}, respectively, in the spectra of copolyurethanes formed using different amounts (% by weight) of DPG. Samples contain ~33% by weight of diacetylene–urethane hard segments and were thermally treated at 100 °C for 40 h: (a) 0% (P[0D20H]), (b) 1.94% (P[5D20H]), (c) 3.62% (P[10D20H]), (d) 5.08% (P[15D20H]). Curves are shifted vertically for clarity.

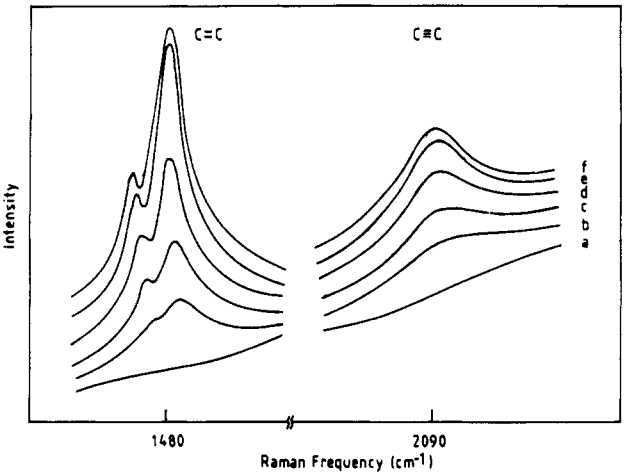


Figure 16. Variations in Raman bands associated with C=C and C≡C stretching modes in the spectra of copolymer P[0D20H] thermally treated at 100 °C for increasing periods of time: (a) as-prepared, (b) 1 h, (c) 5 h, (d) 10 h, (e) 20 h, (f) 40 h. Curves are shifted vertically for clarity.

formation of fewer polydiacetylene molecules and perhaps for shorter polydiacetylene chain lengths being obtained during cross-polymerization. Since the weight fraction of the diacetylene monomer was kept essentially constant in the copolymers formed with various amounts of DPG, and the samples were thermally treated using the same conditions, then similar Raman activities in these samples would be expected if DPG did not alter the copolymer morphology. As discussed previously, the extent of cross-polymerization in the hard segments can be controlled by varying the time and temperature used during thermal treatment. Figure 16 clearly illustrates that the band intensities of the C=C double bond and the C≡C triple bond stretching modes increase steadily for copolymers thermally treated at 100 °C for increasing periods of time, and eventually become constant after about 20 h. Different results were obtained, however, for copolymers subjected to different temperature during thermal treatment over a constant period of time (40 h), as shown in Figure 17. The band intensities first increase as the treatment temperature is increased up to 100 °C, and then decrease as the temperature used is increased from 100 to 160 °C. The decrease in the Raman peak intensities for samples

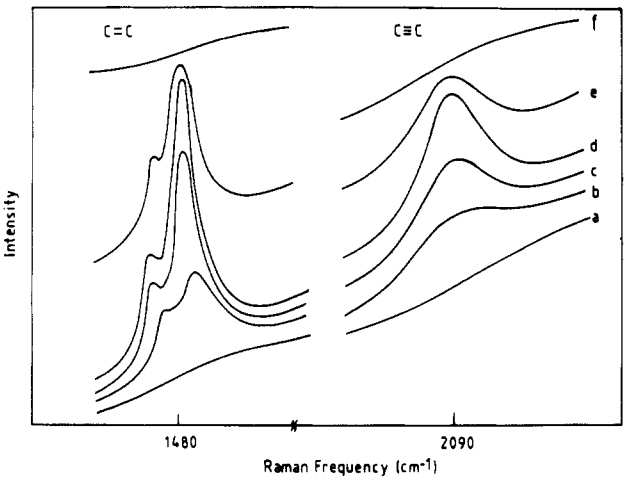


Figure 17. Variations in Raman bands associated with C=C and C≡C stretching modes in the spectra of copolymer P[0D20H] thermally treated for 40 h using increasing cross-polymerization temperatures: (a) as-prepared, (b) 50 °C, (c) 80 °C, (d) 100 °C, (e) 130 °C, (f) 180 °C. Curves are shifted vertically for clarity.

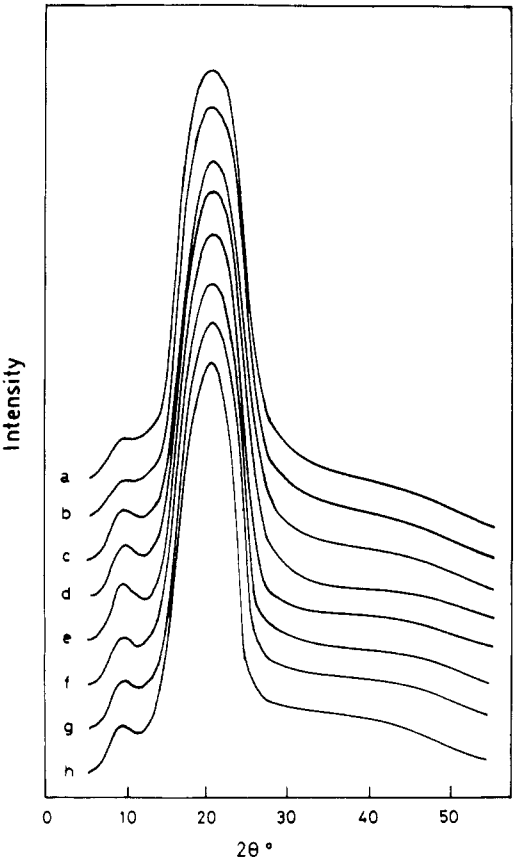


Figure 18. The effects of copolymer composition on the wide-angle X-ray diffraction patterns of thermally treated (100 °C/40 h) copolyurethanes: (a) P[0D0H], (b) P[0D5H], (c) P[0D10H], (d) P[0D15H], (e) P[0D20H], (f) P[5D20H], (g) P[10D20H], (h) P[15D20H]. The diffraction patterns are arbitrarily displaced vertically for clarity.

thermally treated at the higher temperatures is due mostly to the decreasing concentration of polydiacetylene chains formed by solid-state cross-polymerization. As shown by DMTA data, the order–disorder transition of hard-segment domains occurs between 110 to 150 °C so that increasing the thermal treatment temperature above 100 °C reduces the degree of conversion of diacetylene units into resonance Raman-active polydiacetylene chains. Phase mixing and thermal degradation may also cause reductions in the concentration of polydiacetylene chains with corresponding decreases in Raman band intensity. It is found that

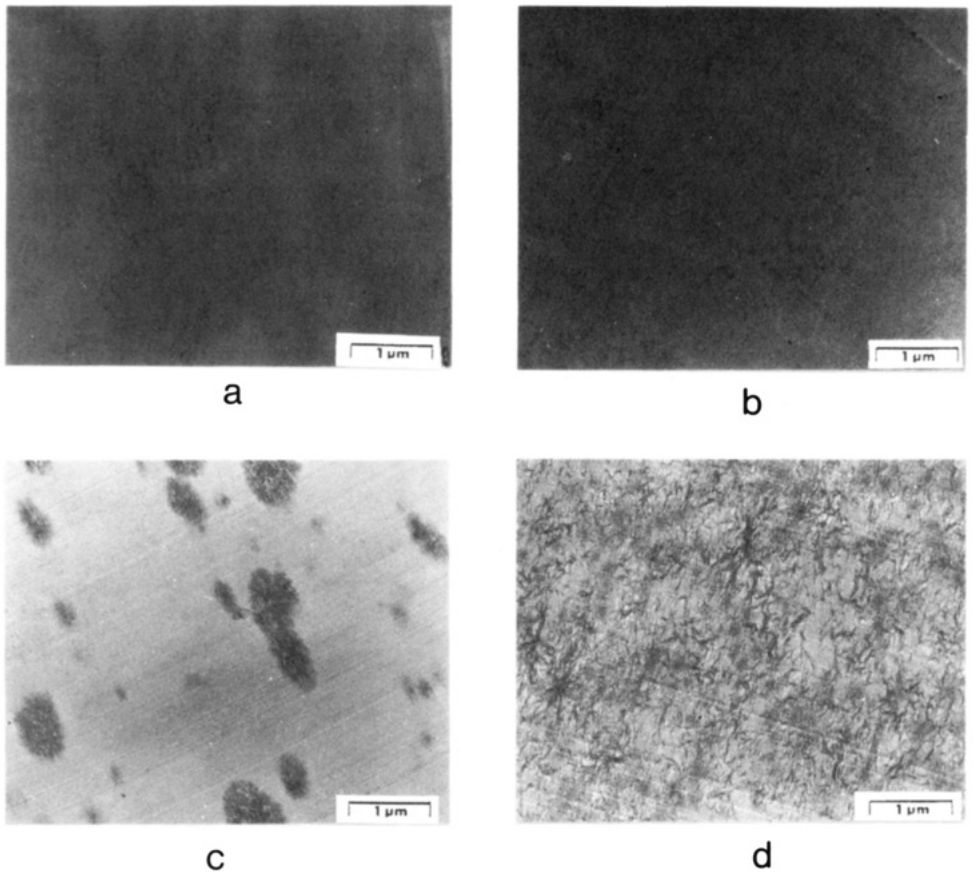


Figure 19. TEM micrographs of thermally treated (100 °C/40 h) copolymers containing different weight fractions of diacetylene-containing hard segments: (a) 12% (P[0D5H]), (b) 19% (P[0D10H]), (c) 27% (P[0D15H]), (d) 34% (P[0D20H]).

the C≡C triple bond stretching band in the copolymer shifts to higher frequency when treated at higher temperature. This may be interpreted by the fact that more significant thermal shrinkage occurs in the material, which leads to the compressive deformation in the polydiacetylene backbones. Generally speaking, the results from Raman spectroscopy provide valuable information about the optical properties of the diacetylene-containing copolymers and the relationships between structure and thermal history of the copolymers. These correlations provide important guidelines which lead to the tailor-making of copolymers with optimum combination of the required optical and other properties.

E. Wide-Angle X-ray Diffraction (WAXD). Wide-angle X-ray diffraction has long been used to examine crystallization in segmented polyurethanes.[22] Figure 18 shows the WAXD diffraction patterns of the diacetylene-containing copolymers of various compositions. Broad amorphous halos are observed at $2\theta \approx 20°$. However, extra weaker peaks are found at $2\theta \approx 9.5°$. It has been suggested that this weak peak corresponds to interference of the hard segments.[23] In fact, it has been established that this interference indicates a quasi-periodic, paracrystalline arrangement of the hard segments and also that it is characteristic of the physical cross-linking shown to be present in linear segmented polyurethanes.[23] All of the copolymers in the present work display similar amorphous halos, whereas the intensity of the weaker peak ($2\theta \approx 9.5°$) increases steadily with increasing HDD content and decreases slightly with the inclusion of DPG in the copolymers. This indicates that differences do occur in the degree of ordering in hard-segment domains in these copolymers.

Small-angle X-ray scattering (SAXS) has also been used[24] to examine the domain structure of the hard segments and to estimate the size scale of the inhomogeneous areas in segmented copolyurethanes. Characterization by SAXS to determine interdomain spacing, interfacial boundary thickness, and degree of segmental mixing in these diacetylene-containing copolymers is currently under investigation and will be reported in a later paper.

F. Transmission Electron Microscopy (TEM). Unstained ultrathin sections (<100 nm thick) of thermally treated copolymers were examined using transmission electron microscopy. The micrographs of the bright-field images are shown in Figures 19 and 20. Almost featureless structures were obtained for copolymer P[0D5H] and P[0D10H], which contain relatively small amounts of HDD. This does not necessarily mean that these two copolymers are totally phase-mixed. On the contrary, they appeared to be highly phase-separated according to the results from thermal analysis (Figure 9). Clearly the hard-segment domains in these two samples are too small or ill-defined to be visualized using TEM under these conditions. For example, when the small domains overlap in the section, they cannot be resolved. However, at high hard-segment content, clearly defined structures are observed even though the samples were not stained. The high-contrast TEM images were obtained due to the large electron-density difference between polydiacetylene-containing hard segments and the completely amorphous poly(ether–urethane) matrix. Spherulitic diacetylene-containing hard domains (≤ 1 μm) are clearly observed to be uniformly distributed throughout the amorphous poly(ether–urethane) phase in copolymers P[0D15H], P[0D20H], and P[5D20H], as shown in Figures 19 and 20. On the other hand, fewer hard-segment domains can be seen in copolymers formed using DPG as the second chain extender. This again gives strong evidence that the inclusion of DPG causes phase mixing and impedes the aggregation of hard segments.

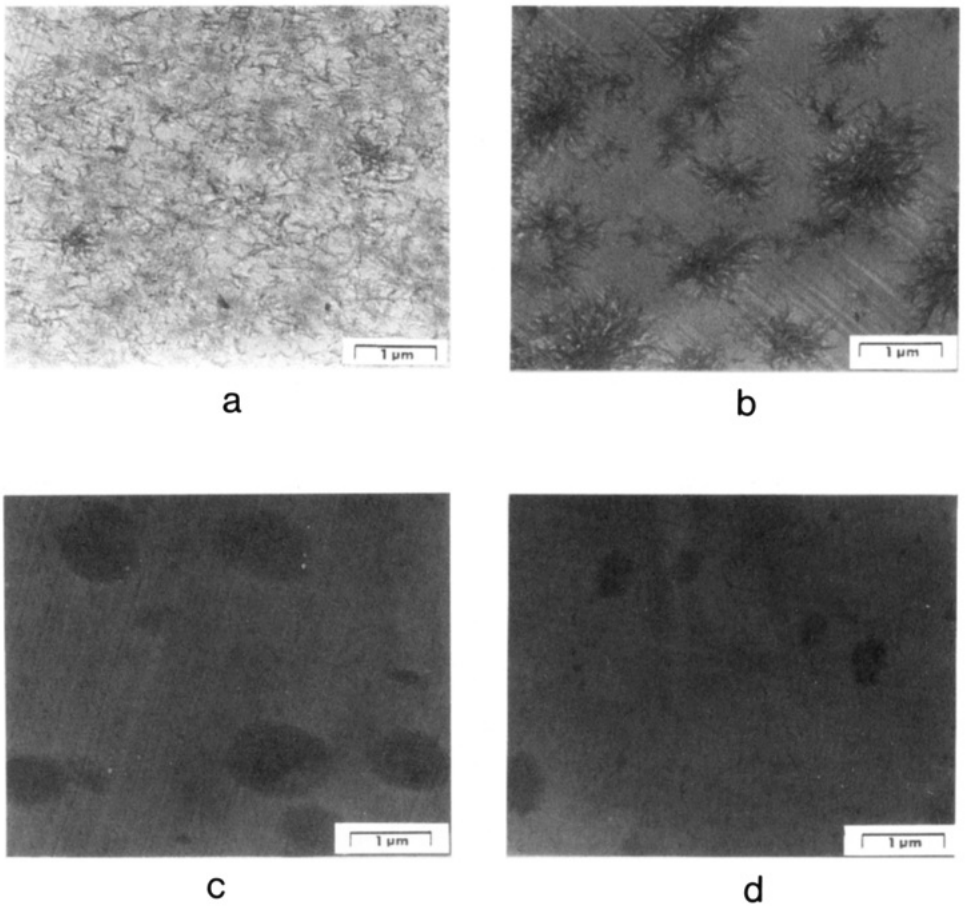


Figure 20. TEM micrographs of copolymers formed using different amounts (% by weight) of DPG. Samples contain ~33% by weight of diacetylene–urethane hard segments and were thermally treated at 100 °C for 40 h: (a) 0% (P[0D20H]), (b) 1.94% (P[5D20H]), (c) 3.62% (P[10D20H]), (d) 5.08% (P[15D20H]).

The morphological features observed in these materials are the result of using a one-shot bulk polymerization process to form copolyurethanes from reactants with substantially different chemical reactivities. The primary hydroxyl groups in HDD are much more reactive toward MDI than the secondary hydroxyl groups in PPG. Initially, therefore, there is an effective excess of MDI over HDD (see Scheme I), so that diacetylene-containing hard segments form perferentially in the early stages of the reaction, with the PPG acting essentially as a polyether solvent. This initial stoichiometric imbalance, defined in terms of the molar ratio of MDI to HDD, decreases from 5 to 2 as hard-segment content increases from 12 to 34%. Applications of the Carothers equation,[25] assuming complete reaction of HDD occurs before reaction of PPG commences, predicts the average degree of polymerization, x_n^H, of the HDD/MDI hard segments to increase from ~1.5 to 3.0. It is known[26,27] that these hard-segment oligomers have strong tendency to aggregate via hydrogen bonding. As the polymerization proceeds, the hard segments will therefore phase separate prematurely by a nucleation and growth process[26,27] to produce large, paracrystalline domain structures. This macrophase separation occurs more readily the greater the value of x_n^H, that is at higher hard-segment content. This leads to formation of the large spherulitic structures observed in Figures 19 and 20. Despite the large domain size, however, it was not possible to obtain well-defined electron-diffraction patterns from the hard segments. This is consistent with the WAXD measurements (Figure 18) and indicates that the spherulitic domains do not have well-defined crystalline structures. However, the hard segments must be sufficiently ordered to allow solid-state cross-polymerization of the diacetylene units to take place. On the other hand, the reaction of PPG-400 (and DPG) with MDI, although relatively slow, must occur during the polymerization and some hard-segment oligomers (isolated and aggregated) become trapped within the polyether-rich phase, and microphase separation undoubtedly occurs but on a much smaller size scale which is not detectable by TEM under the conditions used to obtain Figures 19 and 20. During the final stages of polymerization, reaction between the polyether diol and isocyanate-tipped hard-segment oligomers forming the interfacial regions of the spherulites occurs increasingly and connectivity between the phases then results. Subsequent thermal treatment, in addition to affecting cross-polymerization in the diacetylene-containing phase, completes the hydroxyl–isocyanate reactions, improves phase connectivity, and causes phase boundary mixing,[28,29] all of which result in an overall decrease in phase separation in these copolymers. The more highly aggregated domain structures comprising longer sequences of diacetylene-containing chains would also explain the higher degree (or efficiency) of topochemical cross-polymerization achieved in the higher hard segment copolymers.

Summary and Conclusions

The objective of forming bulk-polymerized, Raman active, glassy copolyurethanes containing phase-separated polydiacetylene domains has been achieved. The extensive understanding of composition (chemical structure)–morphology–property relationships of the diacetylene-containing copolymers should provide general guidelines for designing and tailor-making diacetylene-containing materials with specified optical and mechanical properties and required thermal stability. The one-stage, bulk polymerization process used to produce the initially linear

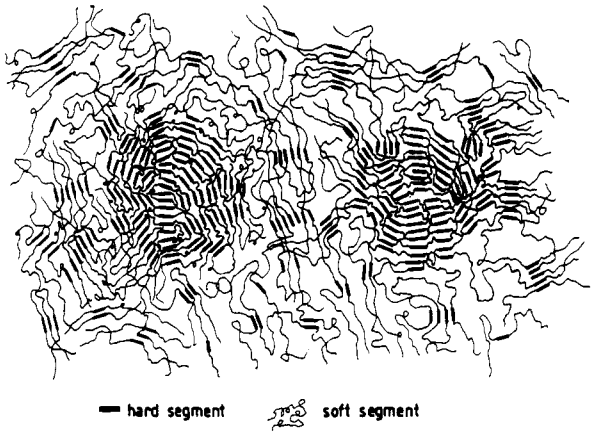


Figure 21. Schematic representation of the microstructural features of a copolymer comprising diacetylene–urethane (HDD/MDI) hard segments dispersed in a continuous, amorphous poly(ether–urethane) (PPG/MDI) matrix.

copolyurethanes has demonstrated additional advantages in terms of the ease of processibility, and their morphologically isotropic nature allows them to be readily processed into variety of forms including fibers, films, bulk sheets, and surface coatings.

The linear copolymer precursors were cross-linked in situ by thermal, solid-state topochemical cross-polymerization of the diacetylene-containing domains to yield intensely colored, insoluble, and infusible materials. The conditions for thermal treatment were optimized at 100 °C/40 h in air, and using temperatures higher than 120 °C caused dissociation of hydrogen bonding in hard-segment domains and thus hindered the solid-state cross-polymerization of diacetylene monomer units. This led to significant loss of resonance Raman activity. Morphologies ranging from the submicron, microphase-separated scale to micron-sized, macrophase-separated spherulites were observed using TEM in copolymers with different compositions. WAXD patterns showed the phase-separated copolymers to comprise paracrystalline, diacetylene-urethane domains uniformly distributed in an amorphous, poly(ether–urethane) matrix. These observations, together with the superstructural evidence provided by transmission electron microscopy, suggest a microstructure for this type of diacetylene-containing copolymers such as that shown schematically in Figure 21.

Incorporation of a second short-chain diol (DPG) during copolymer formation impeded the aggregation of the diacetylene-containing hard segments and severely disrupted the hard-domain structure.

Resonance Raman spectroscopy showed the copolyurethanes to display optical properties similar to those of polydiacetylene single crystals. In particular, similar well-defined resonance Raman spectra of polydiacetylenes were obtained from the copolymers. Raman spectroscopy was found useful in monitoring cross-polymerization reactions and it also gave extra information about the domain structure and phase behavior of the copolymers.

In a subsequent paper,[15] the mechanical and optomechanical behavior of these copolyurethanes will be discussed, and in particular, the molecular deformation of the polydiacetylene chains formed in situ within the HDD/MDI domains, obtained using Raman spectroscopy as the optical microprobe, will be analyzed. The deformation micromechanics so obtained will be correlated with the copolymer structure established in the present paper. The potential application of these copolyurethanes as isotropic, optical stress or strain sensors will be demonstrated.

Acknowledgment. This work was supported by a research grant from the SERC.

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(30) For clarity, all DMTA curves in Figures 9–12 are displaced vertically by one decade for log E' curves and by half a decade for log (tan δ) curves.

Registry No. (MDI)(PPG)(HDD) (block copolymer), 136128-77-3; (MDI)(PPG)(DPG)(HDD) (block copolymer), 137125-42-9.