

# Polyetherurethaneureas Containing Diacetylene in the Hard Segments

S. J. HUANG\* and P. G. EDELMAN,<sup>†</sup> *Department of Chemistry and Institute of Materials Science, Box U-136, University of Connecticut, Storrs, Connecticut 06268*

## INTRODUCTION

The past two decades has seen tremendous growth of interest in the polymers formed from the topochemical reaction of diacetylene containing monomers.<sup>1</sup> In addition to polymerization from monomer, when the diacetylene moiety is incorporated into a polymer backbone, the chains can be crosslinked. Regular network formation is obtained, as opposed to a more random network. The unique properties of these materials were revealed in 1970, when Wegner reported the synthesis of condensation polymers with incorporation of unreacted diacetylene in the backbone.<sup>2</sup>

Diacetylene containing block copolymers that undergo microdomain phase separation have been investigated independently by several groups, including ourselves. Liang and Reiser characterized polyurethane copolymers with diacetylene groups as UV sensitive photopolymers.<sup>3</sup> Proportions of hard and soft segments were varied, as well as the molecular weight and chemical nature. They showed that the extent of microdomain phase association correlated with photocrosslinkability of the diacetylene groups in the hard segment. Rubner has also done extensive investigations of polyether urethanes with diacetylene containing hard segments.<sup>4</sup> In addition to the thermochromic effects noted by many investigators, a strain-induced color change is reported.<sup>4d</sup>

In this report, infrared spectroscopic and differential scanning calorimetric data on new polyetherurethaneureas (PEUUs) are presented. Analogues varying in hard segment content were synthesized from 1,6-diisocyanatohexane (HDI) and 2,4-hexadiyne-1,6-diol (HDD), with an amine-terminated oligoether soft segment consisting of oxyethylene and oxypropylene units. The results indicate that as the hard segment content increased, a higher degree of structural regularity in the hard segment domain was accompanied by increased phase mixing. This morphological change seen by FTIR and DSC is also evidenced by the extent of UV initiated reaction sensitivity.

\*To whom correspondence should be addressed.

<sup>†</sup>Present address: BF-10, Chemical Engineering, University of Washington, Seattle, WA 98195.

## EXPERIMENTAL

### Materials

Propargyl alcohol from General Aniline and Film Co. was vacuum distilled before use. Tetramethylethylenediamine and 1,4-diazabicyclo-[2.2.2]-octane (DABCO) were recrystallized from diethyl ether. Dimethylformamide was shaken over KOH and distilled from CaO. The soft segment was Jeffamine ED-2001, kindly donated by the Jefferson Chemical division of Texaco Chemical.  $^1\text{H-NMR}$  analysis revealed  $\sim 3.3$  propylene oxide end units on either side of  $\sim 40.5$  ethylene oxide units. The molecular weight was 2245 g/mol determined by end-group titration, assuming a functionality of 2.0. The polyether was room temperature vacuum-dried for 48 h just before use. HDI was distilled at reduced pressure. Stannous octoate [tin(II)-2-ethylhexanoate] was used as received from Polysciences. Diethyl ether was reagent grade from Baker and used as received. All other reagents and solvents were purified according to standard procedure.

### Instrumentation

Infrared spectra were recorded on a Nicolet 60SX FTIR using a TGS detector. Thirty-two scans per spectra were signal averaged at a resolution of  $4\text{ cm}^{-1}$ . Samples were prepared by casting thin films from DMF on KBr discs followed by room temperature vacuum drying.  $^1\text{H-NMR}$  was measured at 200 MHz and  $^{13}\text{C-NMR}$  at 50 MHz, both analyzed using an IBM WP-200 SY FT-NMR system.  $\text{CDCl}_3$  and  $\text{DMSO-d}_6$  solutions were used, 3–4% w/w for  $^1\text{H-}$  and 10% w/w for  $^{13}\text{C-NMR}$ . The  $^1\text{H-NMR}$  spectra were averaged from 64 free induction decays (FIDs) whereas the  $^{13}\text{C-NMR}$  spectra were averaged from greater than 10,000 FIDs.

Differential scanning calorimetry (DSC) was performed on an Omnitherm QC-25, at a heating rate of  $20^\circ\text{C}/\text{min}$  on  $10 \pm 1$  mg samples in aluminum pans. Unless otherwise noted, all thermal analysis data reported was from the second heating of the sample after heating to  $100^\circ\text{C}$  followed by immediate quenching with liquid  $\text{N}_2$ . Glass transition temperatures ( $T_g$ ) were taken from the inflection point temperature. Melting points ( $T_m$ ) were taken as the temperature of the endotherm peak minimum. UV irradiation of diacetylene containing PEUUs was done with an Ace-Hanovia 450 W medium pressure mercury vapor lamp with reflector at a distance of  $\sim 25$  cm.

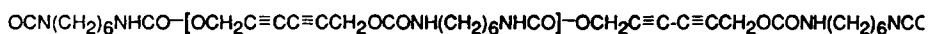
### Synthesis

The synthesis of one polymer composition is described below as being representative of the procedure used for the series (see Reaction Scheme 1). HDD (2.90 g, 26.3 mmol), synthesized by the method of Hay,<sup>5</sup> was recrystallized twice from toluene before use, and then dissolved in 10 mL DMF with catalytic amounts of DABCO (0.0042 g, 0.04 mmol) and stannous octoate (0.129 g, 0.03 mmol). One half of the total amount of HDI (total amount was 4.99 g, 29.0 mmol) was mixed in 5 mL of DMF and slowly added to the HDD solution stirring in a 100-mL three-necked round-bottom flask equipped with argon purge, thermometer, and magnetic stir bar. After 45 min the other half

of the HDI solution was added dropwise to the reaction mixture at room temperature. Five hours later the polyether (5.020 g, 2.23 mmol) which had been dissolved in 20 mL of DMF was added dropwise to the mixture. Aliquots were withdrawn at intervals during the polyether addition and checked via infrared for extent of reaction. In all cases the isocyanate band disappeared completely before the full stoichiometric equivalent of polyether had been added, at which point the addition of DMF was terminated. By this point, considerable thickening occurred hence. More DMF was added to facilitate uniform mixing. The product was precipitated from diethyl ether, rinsed five times in methanol and vacuum dried at room temperature for 48 h.

## RESULTS AND DISCUSSION

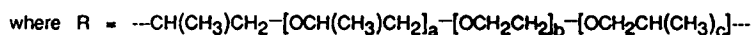
Conventional microdomain phase separated hard/soft segment polyetherurethanes and polyetherurethaneureas can be made by a two-step solution process to obtain a sequence distribution of hard/soft segments more closely approximating the initial reaction stoichiometry. In the first step, the diisocyanate is reacted with the soft segment oligomer to ensure complete endcapping. In the second step, a more reactive low molecular weight diol or diamine reacted with the isocyanate end groups to extend the chain length. In the present work, the diisocyanate was first reacted with the low molecular weight diacetylene diol to compensate for its lower reactivity, and to insure a high level of diacetylene incorporation:



I



II



$$a + c = 6.7 \text{ and } b = 40.5; \text{ MW} = 2245 \text{ g/mol}$$

Scheme 1

In the second step, the isocyanate end-capped hard segment was reacted with an oligomer containing more reactive aliphatic amine end groups. The feed

TABLE I  
 PEUU Feed and Product Molar Ratios

Sample	Initial mole ratios			<sup>1</sup> H-NMR results		
	HDI	HDD	ED-2000	HDI	HDD	ED-2000
PEUU-1:1:0	1.01	1.00	0	1.1	1.0	0
PEUU-64:48:1	225	201	1.00	64	48	1.0
PEUU-19:12:1	13.0	11.8	1.00	19	12	1.0
PEUU-5.3:2.9:1	4.50	3.41	1.00	5.3	2.9	1.0
PEUU-2:1:1	2.48	1.12	1.00	2.2	1.0	1.0

 TABLE II  
 Infrared Absorbances of Diacetylene Containing Polyetherurethaneureas

Sample	$\nu(\text{NH})$	$\nu(\text{C}=\text{O})$			$\nu(\text{C}-\text{N})$
		$\text{UT}_f$	$\text{UT}_b$	UR	
PEUU-2:1:1	3300	1725	—	1633	1555
PEUU-5.2:2.9:1	3321	1727	—	1662	1535
PEUU-19:12:1	3311	1720	1693	1661	1542
PEUU-1:1:0	3316	—	1696	1667	1541

$\text{UT}_f$  = free urethane  $\nu(\text{C}=\text{O})$ ,  $\text{UT}_b$  = bonded urethane  $\nu(\text{C}=\text{O})$ , all values in  $\text{cm}^{-1}$ .

mole ratios and product mole ratios (via <sup>1</sup>H-NMR) are shown in Table I. The numbers used for sample designations indicate the mole ratios of diisocyanate:diacetylene:polyether as determined by <sup>1</sup>H-NMR peak integration. Possible reasons why feed mole ratios do not correspond to product mole ratios are believed to be primarily due to impurities in the polyether. These reasons have been discussed in greater detail elsewhere.<sup>6</sup>

To initially characterize these polymers after synthesis, their infrared spectra were recorded. Selected band assignments are given in Table II. The nonpolar diacetylene groups, being infrared inactive, were not in evidence in these spectra. From the spectrum of the hard segment model (PEUU-1:1:0) in Figure 1, definite peaks can be assigned with relative certainty. There is a very sharp urethane  $\nu(\text{NH})$  band at  $3316 \text{ cm}^{-1}$  and a narrow absorption band for the urethane  $\nu(\text{C}=\text{O})$  at  $1696 \text{ cm}^{-1}$ . Also evident is a sharp  $\nu(\text{O}=\text{C}-\text{NH})$  peak at  $1541 \text{ cm}^{-1}$ . These frequency values clearly point to the fact that the  $\text{C}=\text{O}$  and  $\text{NH}$  groups are hydrogen-bonded to each other.<sup>7,8</sup> The shape of the  $\nu(\text{NH})$  and  $\nu(\text{C}=\text{O})$  peaks suggest uniformity of hydrogen bond distances.<sup>9</sup> This implies a high degree of structural regularity, as seen with diacetylene monomers with urethane side groups in the unreacted crystalline state.<sup>10</sup> Regular packing enhances the diacetylene reactivity, as seen by the relative UV sensitivity.<sup>3,6</sup>

For the hard segment model polymer, a situation not unlike the idealized case depicted in Figure 2 can be envisioned. The regular packing is analogous to that deduced from studies of low molecular weight diacetylene monomers. Exposure to high energy radiation, such as UV light, can induce the solid state topochemical reaction of the rodlike diacetylene moieties, whereupon the reactive centers may rotate on their axes during the reaction.

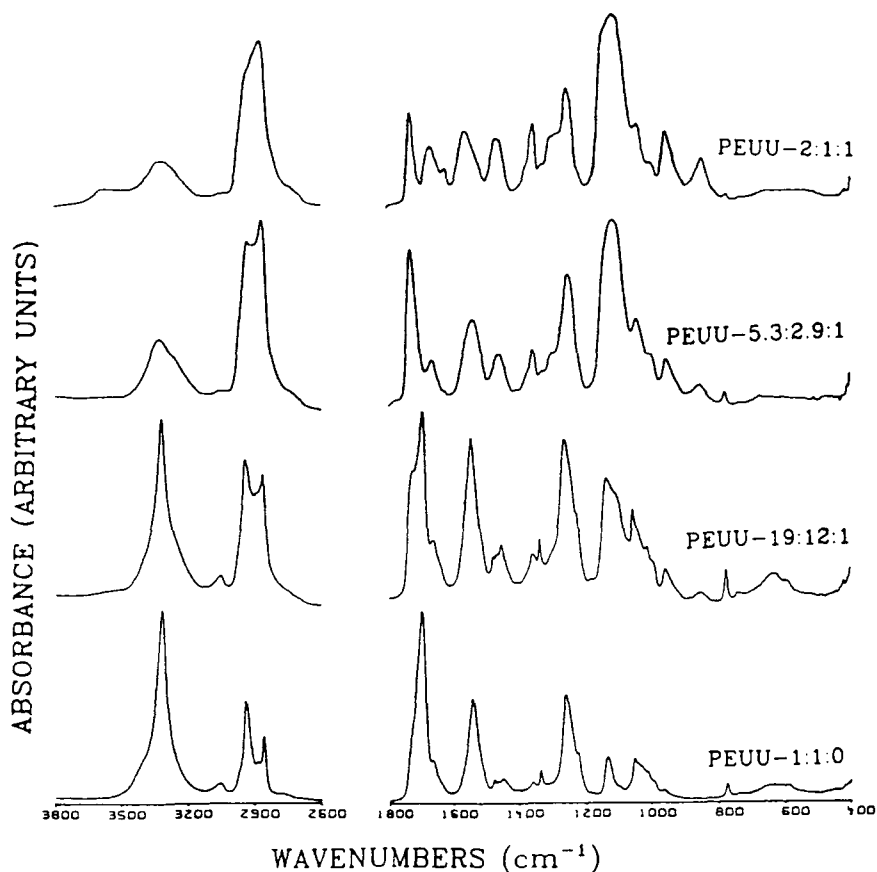


Fig. 1. Infrared absorbance spectra of diacetylene containing poly(ether urethane urea)s.

But the spectra indicate that there are imperfections in the regularity. The small high energy shoulder of the NH peak indicates either nonbonded or urea protons. A small carbonyl peak at  $1667\text{ cm}^{-1}$  in connection with NMR data published elsewhere<sup>6</sup> strongly suggests the presence of urea groups resulting from side reactions occurring due to the presence of trace amounts of  $\text{H}_2\text{O}$ .

In the spectrum of PEUU-19:12:1 there are changes in the carbonyl region which are not reflected in the NH portion of the spectrum. A significant shoulder at  $1720\text{ cm}^{-1}$  can be assigned to free urethane carbonyl. The bonded urethane carbonyl has shifted slightly to lower energy at  $1693\text{ cm}^{-1}$ . The  $\nu(\text{NH})$  peak at  $3311\text{ cm}^{-1}$  has not significantly changed its shape. This suggests that oxygen of the polyether block has partially filled the role of hydrogen bond acceptor, but the majority of the urethane protons are still bonded at uniform distance from the urethane  $\text{C}=\text{O}$ . The ether  $\nu(\text{C}-\text{O}-\text{C})$  band at  $1110\text{ cm}^{-1}$  and a peak for the urea carbonyl at  $1661\text{ cm}^{-1}$  are also apparent.

In the PEUU-5.3:2.9:1 spectrum the urethane carbonyl appears completely nonbonded at  $1727\text{ cm}^{-1}$  with significant broadening of the  $\nu(\text{NH})$  band. The broadening indicates more diverse states of hydrogen bonding. The

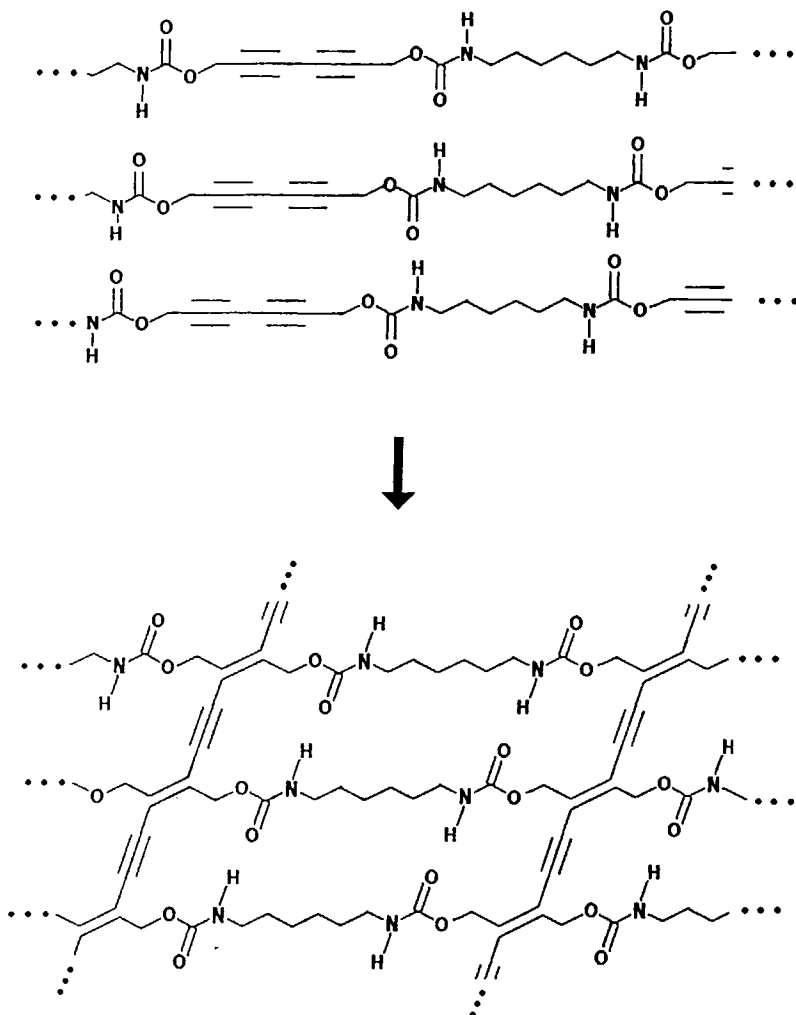


Fig. 2. Idealized schematic illustrating topochemical reaction occurring during solid state crosslinking of diacetylene containing poly(ether urethane ureas).

$\nu(\text{O}=\text{C}-\text{NH})$  band at  $1535\text{ cm}^{-1}$  has also broadened considerably. The urea  $\nu(\text{C}=\text{O})$  peak is more distinct at  $1662\text{ cm}^{-1}$  since the bonded urethane carbonyl has been replaced by the nonbonded  $\nu(\text{C}=\text{O})$ .

In the spectrum of PEUU-2:1:1 there is a peak for nonbonded urethane at  $1725\text{ cm}^{-1}$ , urea peak at  $1633\text{ cm}^{-1}$ , and a new peak at  $1618\text{ cm}^{-1}$  of unclear origin. Evaluation of the  $\nu(\text{NH})$  absorption signal peak position suggests that the majority of NH protons are bonded. The broad peak at  $3567\text{ cm}^{-1}$  is most likely due to amine end groups, as the free urea or urethane  $\nu(\text{NH})$  band absorbs close to  $3400\text{ cm}^{-1}$ . Since the urethane carbonyl indicates a total lack of hydrogen bonding, the urethane NH protons must be bonded to the ether oxygens of the soft block. The diacetylene segments appear to be completely dissolved in the polyether segment.

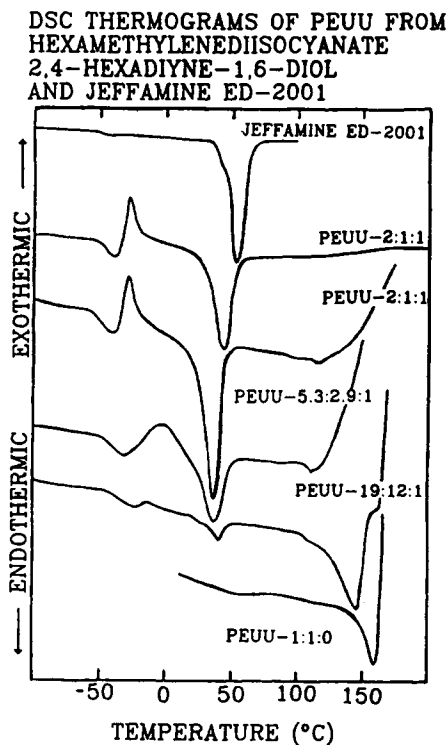


Fig. 3. Differential scanning calorimetry scans for diacetylene containing poly(ether urethane ureas).

Moderate compatibility between the soft and hard segments is indicated by this infrared study. As the composition increases in soft segmented content, the polyether provides an increasing source of proton acceptor, indicated by the decreased intensity shift of the bonded carbonyl in favor of the nonbonded C=O. The NH peak maintained the low energy hydrogen bonded position with broadening. The concurrent carbonyl shift to a nonbonded energy suggests a shift from partial microdomain phase separation to complete phase mixing.

The interesting properties and trends seen by FTIR investigation are confirmed by analysis of the thermal properties of these materials. Figure 3 shows the DSC scans for the series of PEUUs. The soft segment  $T_g$  increases from  $-52$  to  $-37^\circ\text{C}$  as the composition goes from 100 to 30% of the polyether (by weight) as shown in Figure 4. The diacetylene segments are soluble in the polyether, shown earlier from the FTIR results. As more hard segment is incorporated into the PEUU, more hard segment dissolves in the soft domain. As has been observed with other hard/soft segment poly(ether urethane)s, when hard segment content increases, not only is there more separated hard segment domain, but also more hard segment dissolved in soft segment domains.<sup>11</sup> This may cause an increase of the soft phase  $T_g$  for two reasons. One cause of increase, due to miscibility of the two phases, should follow the Fox-Flory equation.<sup>12</sup> If this does not fully account for the increase, there

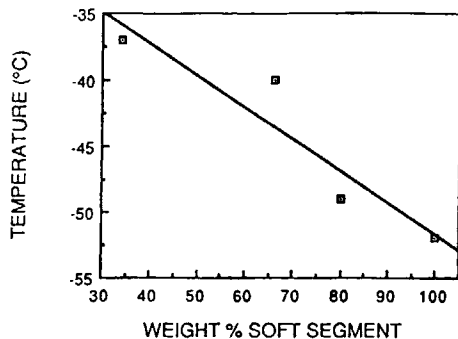


Fig. 4. Decrease in soft segment  $T_g$  with increase in soft segment content.

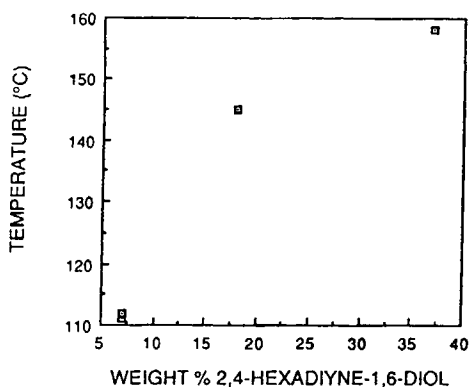


Fig. 5. Increase in hard segment  $T_m$  with increasing hard segment content.

may also be a contribution from hydrogen bonding of the urethane NH to the polyether oxygens, which act as crosslinks.<sup>8</sup> In order to study this more fully, the hard block  $T_g$  would have to be determined. However, it was not unambiguously detected in this work. The increasing hard segment melt temperature with hard segment content is due to an increase in hard segment molecular weight, as shown in Figure 5.

In all samples exhibiting a hard segment melt, there is also a marked exotherm which begins right after the hard segment melt, seen in Figure 2. This is due to the exothermic reaction of the diacetylene groups. Wherein the polymer is crosslinked after the diacetylenes react. It is interesting that this thermally excited reaction occurs in the melt, when little ordering of the diacetylenes exists.

## CONCLUSION

This article has presented FTIR and DSC data on a novel series of analogous poly(ether urethane ureas) that vary in hard segment content. The PEUUs exhibit composition dependent morphology. On one extreme the behavior can be described as phase separated with some diacetylene dissolved in polyether. It is noted that domain separation is never complete, as indicated by the increase in the soft segment  $T_g$ . However, at high hard segment contents there



is remarkable uniformity of hydrogen bonded states, shown by the narrowness of the IR peaks for both NH and C=O bond. At the other extreme, the low hard segment content PEUU shows complete mixing of the urethane segments in the polyether. This morphology can be seen to affect diacetylene reactivity. The more phase separated those compositions which phase separated also display increased thermal and photoreactivity. However, when the  $-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$  group is completely dissolved at low concentration, there is no apparent reactivity.

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Received July 28, 1988

Accepted August 3, 1988