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Synthesis and Physical Properties of Liquid Crystalline Alkyl Isocyanate Copolymers

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ABSTRACT: A series of alkyl isocyanate homopolymers and copolymers were synthesized to investigate the influence of alkyl chain length on physical and chemical properties, especially decomposition behavior. In a series of undecyl isocyanate copolymers containing 50 mol % of ethyl, propyl, butyl, hexyl, and octyl isocyanate, a mild upward trend was found for the clearing temperature, whereas the crystal-to-nematic transition temperature remained unchanged at about 108 °C. Glass transitions were also found; they fell and then rose as the comonomer chain length increased. Thermal gravimetric analysis showed that copolymerization provided no improvement in stability; all polymers decomposed at around 180 °C. However, the isotropic temperature range is improved by copolymerization due to the depression of the clearing temperature.

Introduction

Liquid crystal polymers (LCP's) have wide applications ranging from electronic devices to ultra-high-strength materials. These intriguing polymers have been the subject of several review articles.[1-3] Of the polymeric liquid crystal systems, poly(alkyl isocyanates) are categorized as main-chain mesogenic polymers having a semi-rigid structure. Though the synthesis and characterization of poly(alkyl isocyanates) were originally reported by Shashoua et al.,[4,5] the liquid crystalline nature of these systems was investigated in greater detail by Aharoni and co-workers.[6-11] These studies, involving various alkyl and aromatic isocyanate polymers, showed that while the alkyl isocyanate homo- and copolymers exhibited thermotropic liquid crystalline behavior, they decomposed spontaneously above their melting points. Because of this decomposition property, the use of poly(alkyl isocyanates) as thermotropic liquid crystals is limited.

The aim of our study of poly(alkyl isocyanates) was to improve their utility as model thermotropic LCP's; in particular, to widen the isotropic region without destroying their liquid crystallinity or solubility. A wide isotropic region is necessary for comparative rheological studies, for example. From the results of Shashoua[5] and Aharoni[6,10,11] it was known that the temperature of melting (T_m) decreases in poly(alkyl isocyanates) when the alkyl chain length of the monomer increases because the volume of the side chains prevents the highly polar main chains from packing closely. Moreover, copolymers of butyl isocyanate with ethyl isocyanate[12,13] and butyl isocyanate with (p-methoxyphenyl)-3-propyl isocyanate[10] (50:50 mol ratio) were reported to exhibit increased thermal stability and a wider range of mesmorphicity, respectively, than the corresponding homopolymers.

From these studies, it was considered probable that the introduction of irregularity into the side chains would lower the clearing temperature without changing the decomposition temperature. The irregularity can be achieved by synthesizing copolymers from long aliphatic side chain monomers with monomers containing shorter chains. We chose undecyl isocyanate as our base polymer because it appears to be the upper limiting case of transition from mesogenic to nonmesogenic polymers. Here we report the synthesis of homopolymers and 50:50 copolymers of undecyl isocyanate with propyl, butyl, hexyl, and octyl isocyanates using anionic initiation with NaCN. These polymers were characterized using FT-IR, TGA, DSC, thermal optical analysis (TOA), dynamic mechanical analysis (DMA), and tensile testing.

Experimental Section

Materials. *n*-Propyl isocyanate (Aldrich), *n*-ethyl isocyanate (Aldrich), *n*-hexyl isocyanate (Kodak), *n*-octyl isocyanate (Kodak), *N*,*N*-dimethylformamide, and toluene were distilled from calcium hydride before use. The *N*,*N*-dimethylformamide was stored over molecular sieves. The initiator was prepared from the freshly distilled *N*,*N*-dimethylformamide and sodium cyanide as a saturated solution. Undecyl isocyanate

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was synthesized from lauryl chloride (Aldrich) by the method of Boehmer[14] as described below.

Synthesis of Undecyl Isocyanate. Into a 2-L round-bottom flask fitted with a long condenser and a calcium chloride guard tube, 173 mL of lauryl chloride (0.75 mol) was added slowly to 280 mL of toluene containing 65 g of sodium azide (1.0 mol) already in the flask. The reaction mixture was slowly heated with constant stirring to a point of gentle reflux and then allowed to reflux for about 8 h until no further nitrogen evolved. It was then cooled to room temperature and the solid material was filtered out. The solvent was evaporated and the monomer was purified by vacuum distillation.

Synthesis of Copolymer. Into a 500-mL three-necked round-bottom flask fitted with a mechanical stirrer and serum septa, nitrogen gas was introduced by means of a syringe needle. Before adding the monomer and solvent into the reaction flask, the flask was heated with continuous nitrogen gas purge to remove the trace amount of moisture present in the system. Then 50 mL of *N*,*N*-dimethylformamide, 7.9 g of undecyl isocyanate (0.04 mol), and 3.4 g of propyl isocyanate (0.04 mol) were introduced into the reaction flask through a syringe needle. (When the polymerization reaction was tried with 50:50 volume of dimethylformamide and toluene, no polymer precipitated out after the initiator was added.) The reaction mixture was cooled externally by using a dry ice–acetone bath. When the reaction mixture became solid, the dry ice–acetone bath was slowly removed in order to stir the contents. As soon as the solid dissolved, the dry ice–acetone bath was introduced once again. This procedure was repeated several times with constant stirring and continuous nitrogen purge. The above process was designed to remove any dissolved oxygen in the reaction mixture. While keeping the reaction mixture just above the melting point of dimethylformamide (−58 °C), 2 mL of initiation solution (NaCN in DMF) was injected with vigorous stirring. The polymer precipitated immediately from the reaction medium but was allowed to stand at dry ice–acetone temperature for 5 min after the initiator was added. Finally, methanol was added and the polymer was filtered and washed with methanol several times. The polymer was dried in a vacuum oven at 50 °C for 3 days.

Preparation of Polymer Films. Thin uniform films of the polymers were cast on glass plates from chloroform solutions. Films, 0.05–0.14 mm thick, were dried first at room temperature and finally at 50 °C for 2 days in a vacuum oven before mechanical testing.

Characterization. Infrared spectra were taken by using films cast from chloroform on NaCl plates in a Nicolet-60SX Fourier transform infrared spectrometer. To improve signal to noise, 32 scans were averaged. Background spectra were subtracted from the specimen spectra before recording.

A Du Pont Model 950 thermal analyzer was employed for thermogravimetric analysis (TGA). A sample of $\sim$20 mg was heated at 20 K/min in a nitrogen atmosphere. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer DSC-2 attached to a data station and printer. The specimens were heated at a rate of 20 K/min in nitrogen.

Thermal optical analysis measurements were carried out on thin films sandwiched between microscope slides and observed with a polarizing binocular microscope equipped with a stabilized light source, a heated stage, and a photodetector on one ocular. The intensity of the light was recorded as a function of temperature. The instrument was calibrated with naphthalene and adipic acid.

The thermal transitions of the undecyl isocyanate copolymers were measured with a Du Pont Model 990 DSC instrument at 20 K/min in nitrogen. Indium was used for temperature calibration. In most cases an additional run was performed by heating a fresh specimen to 60 °C at a heating rate of 20 K/min and quenching to 110 °C with liquid nitrogen; it was then scanned at 20 K/min.

Dynamic mechanical analyses were conducted on cast films with a Rheovibron DDV II viscoelastometer at 11 Hz. The temperature was raised by manual control at a rate of $\sim$1 K/min.

Tensile tests were performed on an Instron instrument at 23 °C by using a strain rate of 100%/min. Test specimens in the form of strips were cut from the dried polymer film samples.

Table I
Synthesis of Poly(undecyl isocyanate) and 50:50 Copolymers

polymer	abbreviation	yield, %	η_{inh}[a]
poly(undecyl isocyanate)	PUNI	79	3.96
poly(undecyl isocyanate-*co*-ethyl isocyanate)	PUNETI		
poly(undecyl isocyanate-*co*-propyl isocyanate)	PUNPRI	67	8.90
poly(undecyl isocyanate-*co*-butyl isocyanate)	PUNBUI	73	4.89
poly(undecyl isocyanate-*co*-hexyl isocyanate)	PUNHYI	66	10.77
poly(undecyl isocyanate-*co*-octyl isocyanate)	PUNOCI	75	3.58

[a] Inherent viscosity determined in toluene at 25 °C with a concentration of 0.1 g/dL.

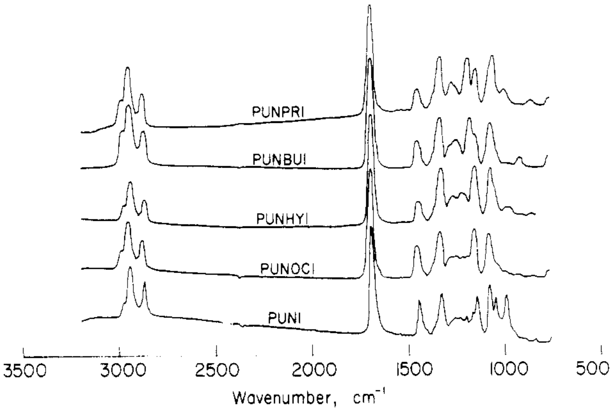

Figure 1. Infrared spectra for poly(undecyl isocyanate) (PUNI) and its copolymers with propyl (PUNPRI), butyl (PUNBUI), hexyl (PUNHYI), and octyl (PUNOCI) isocyanate.

Results and Discussion

The purity of the undecyl isocyanate was confirmed by the complete disappearance of the IR absorption band at $\sim$1800 cm^{-1} and the appearance of a very strong absorption band at $\sim$2275 cm^{-1} corresponding to COCl and NCO, respectively. The composition of the monomers in the feed was 50:50 mol ratio and was assumed to be the same in the copolymers. This assumption was checked on selected copolymers by elemental analysis; the most extreme copolymer, ethyl/undecyl, gave 0.48, 0.42, and 0.30 mol fraction ethyl content by N, C, and H analysis, respectively. The sequence distribution of the conomoners was not resolved by NMR (400 MHz) but was inferred to be random from the mass analysis of trimers from the pyrolysis of the copolymers.[15] The yields of the polymers are given in Table I.

The results of the IR spectral analyses of poly(undecyl isocyanate) and copolymers are given in Figure 1 and Table II. The C=O stretching frequency was found to be essentially independent of the copolymer composition. The IR spectra of poly(undecyl isocyanate) reported by Aharoni[6] showed a strong carbonyl doublet (1685 and 1695 cm^{-1}). In contrast, for the same polymer, we observed only one strong absorption band at $\sim$1697 cm^{-1}. The absorption bands at $\sim$1075 cm^{-1}, corresponding to C–N stretching, gradually shifted to higher wavenumber when the monomer was changed from propyl to octyl isocyanate. Similarly, it was found that there were noticable irregular changes occurring in the absorption region between 1160 and 1390 cm^{-1}, corresponding to the disubstituted amide structure[16] and other bands. The strong absorption band observed for poly(undecyl isocyanate)

Table II
Infrared Analysis of Poly(undecyl isocyanate) Copolymers

	absorption wavenumbers, cm^{-1} (intensities[a])				
polymer	C=O stretch	C—H stretch	C—H bend	C—N stretch	disubstituted amide and other bands[b]
PUNPRI	1699	2930 (0.56) 2860 (0.31)	1459 (0.21)	1079 (0.47)	1207 (0.46) 1271 (0.22) 1286 (0.26) 1347 (0.49)
PUNBUI	1699	2925 (0.57)	1462 (0.25)	1089 (0.41)	1194 (0.46) 1270 (0.25) 1292 (0.21) 1347 (0.46)
PUNHYI	1698	2924 (0.37)	1469 (0.19)	1095 (0.41)	1180 (0.48) 1226 (0.24) 1241 (0.25) 1285 (0.22) 1346 (0.48)
PUNOCI	1698	2930 (0.45) 2855 (0.28)	1470 (0.30)	1097 (0.41)	1171 (0.45) 1227 (0.20) 1269 (0.20) 1286 (0.20) 1346 (0.43)
PUNI	1697	2921 (0.53) 2851 (0.34)	1466 (0.33)	1075 (0.39)	1168 (0.39) 1224 (0.20) 1264 (0.09) 1286 (0.17) 1347 (0.39)

[a] Intensities relative to C=O stretch are given in parentheses. [b] See ref 15 for assignment.

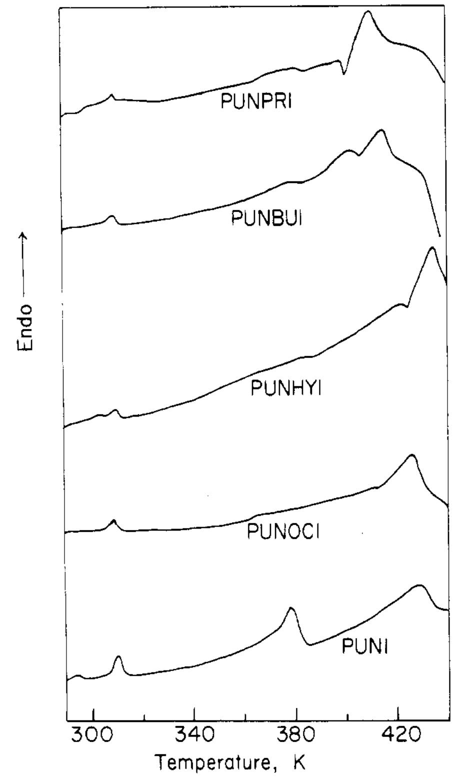

Figure 2. DSC melting transitions of poly(undecyl isocyanate) and its copolymers. Abbrevations are as in Figure 1 and Table I.

at 1101 cm^{-1} was not observed in all the copolymer systems.

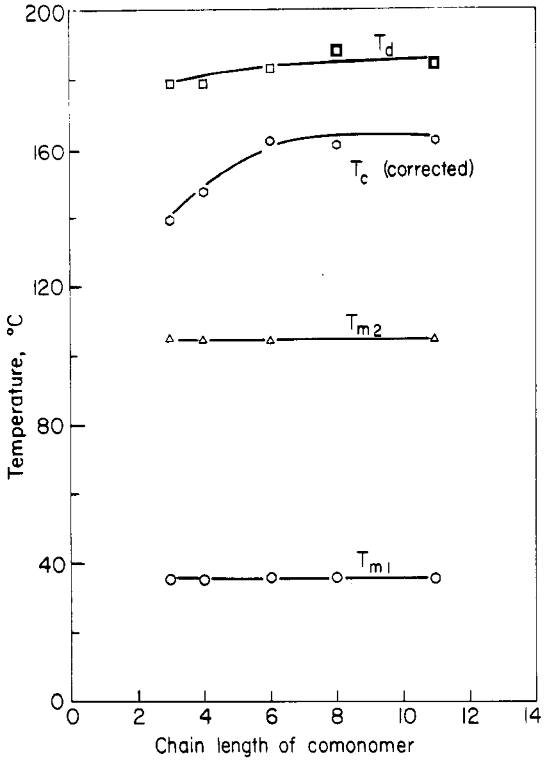

Figure 3. Summary of melting, clearing, and decomposition temperatures for undecyl isocyanate copolymers.

Table III
Transition Temperatures of Poly(undecyl isocyanate) Copolymers

	DSC transitions,[a] °C					
polymer	T_{m_1}	T_{m_2}	T_c	T_d	$T_d - T_c$	T_c (TOA)
PUNPRI	35.7	104.5	137 (139)	179	42 (40)	172
PUNBUI	35.8	104	142 (147)	179	37 (32)	175
PUNHYI	36.2	103.8	162 (163)	184	21 (21)	182
PUNOCI	36.0	b	153 (161)	189	35 (26)	185
PUNI	35.8	104	155 (163)[c]	183	28 (20)[c]	170

[a] T_{m_1} = lower melting transition; T_{m_2} = solid to liquid crystalline transition; T_c = liquid crystalline to isotropic transition; T_d = decomposition temperature. [b] Not observed. [c] Corrected for molecular weight. The corrections were based on the assumption that the concentration of the solutions was dilute enough to assume $\eta_{inh} = [\eta]$ and that the MW dependence of T_c followed that of poly(hexyl isocyanate) reported by: Krigbaum, W. R.; et al. *Macromolecules* **1985**, *18*, 973.

The DSC results of poly(undecyl isocyanate) and its copolymers are presented in Figures 2 and 3 and in Table III. These results are taken from the sound scan after heating to 100 °C and quenching back to −20 °C. Scans of the virgin polymer showed, in addition to other transition peaks observed for all the poly(undecyl isocyanate) copolymers, an endothermic peak at ~72 °C (peak maximum) for poly(undecyl isocyanate) and an undecyl/octyl copolymer. However, in the second scan, this endotherm disappeared, while the other transitions were unaffected; it was therefore hypothesized that the 72 °C peak was a result of the solvent casting process.

In all the DSC curves, the endothermic transition at ~36 °C may be due to the melting of the long aliphatic side chains. The melting of the side chain was not affected by the presence of comonomer in the copolymer, as evidenced from the constant transition temperatures observed for all the homo- and copolymers. Loss of three-dimensional order of the main chains is hypothesized to occur at the second transition listed in Table III.

Aharoni[10] stated that since thermal decomposition of some polyisocyanates may set in at a temperature significantly lower than the clearing temperature (T_c), the T_c of these polymers may not be observable with DTA or DSC. Though he observed the T_c transitions from DTA-DSC analysis for butyl, hexyl, and octyl isocyanate homopolymers, he did not observe any T_c for poly(undecyl isocyanate) homopolymers. Our DSC results

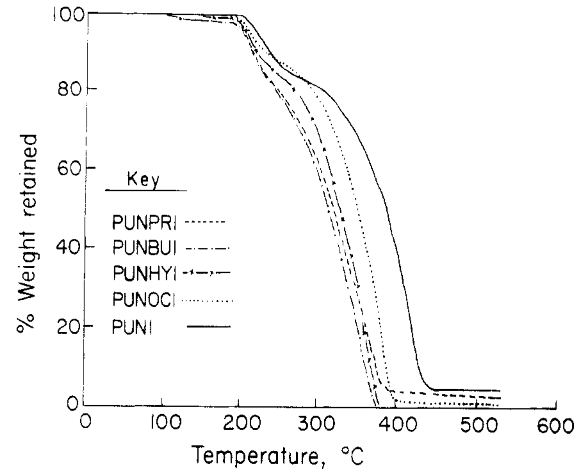

Figure 4. Thermogravimetric analyses of undecyl isocyanate copolymers. Abbreviations are listed in Table I.

from both types of experiments clearly indicate a clearing transition. This result itself suggests that the polymer does not undergo decomposition before the melting of the liquid crystal. The clearing transition was observed in all the copolymers as well. The temperature difference between the clearing temperature and decomposition provides a measure of the range of the isotropic state for these polymers. By varying the comonomer from undecyl to propyl isocyanate, this difference in temperature (Figure 3) increased from $\sim$20 to 40 °C. Thus the introduction of comonomer produces materials with a practical temperature range for studying the isotropic state of these liquid crystalline systems. This improvement is due mainly to a decrease in the clearing temperature of the copolymer (Figure 3).

The clearing points observed from the thermal optical analysis are given in Table III and are found to increase when the comonomer was varied from propyl isocyanate to octyl isocyanate. With the exception of poly(undecyl isocyanate) itself, this increasing trend is in agreement with the T_c observed from the DSC analysis. We do not have an explanation for the descrepancy in the case of the homopolymer. In general, an increase in T_c of the polymer systems can be achieved either by increasing the interaction of the chains or by increasing the rigidity of the main chain.[17,18] Both effects might be achieved by introducing groups that can form intra- or intermolecular hydrogen bonds. For acrylate polymers, the observed effect of pendant groups on T_g, which is sensitive to similar factors, is that T_g decreases with increasing length of side chain until the length reaches eight carbons and increases after this.[19] We would thus expect a decrease of T_c on increasing the alkyl chain length in a series of poly(alkyl isocyanate) homopolymers, and this has indeed been reported.[5,6,10]

The decrease of T_c on decreasing the alkyl chain length of one-half of the side chains of a dodecyl isocyanate copolymer is again probably entropic in origin, but in this case the largest contribution is a gain in entropy of the crystal as the size descrepancy between each comonomer increases. This is commonly observed with the addition of small amounts of foreign comonomer into crystalline polymers; e.g., propylene into polyethylene.

The thermal stabilities of these polymers, as found with TGA analysis, are presented in Figure 4 and Table IV. The initial decomposition of these polyisocyanates was observed to start at $\sim$460 K (190 °C), in agreement with the DSC. Moreover the shapes of the curves demonstrated that the rate of decomposition was faster for the copolymer than for the homopolymer, once the process began. An additional feature was a two-stage decomposition. All the polymers underwent complete decomposition at $\sim$450 °C.

Table IV
Thermogravimetric Analysis of Poly(undecyl isocyanate) Copolymers

	temperatures, °C, corresponding to		
polymer	initial decomp	25% weight loss	>98% weight loss
PUNPRI	190	250	440
PUNBUI	190	250	370
PUNHYI	195	270	380
PUNOCI	190	300	430
PUNI	195	310	450

Table V
Glass Transition Temperatures Observed for Poly(undecyl isocyanate) and Copolymers

polymer	DSC, °C	rheovibron, °C
PUNI	-16.5	-14.0
PUNETI	-32.1	-25.0
PUNPRI	-34.0	-32.0
PUNBUI	-39.5	-40.0
PUNHYI	-43.1	-40.0
PUNOCI	-36.7	-24.0

Because many mechanical and physical properties change in the neighborhood of the glass transition temperature (T_g), it is very important to determine the T_g of these liquid crystalline polymers. Though Aharoni[6] reported the glass transition temperatures for some of his poly(alkyl isocyanates), he also mentioned that occasionally observed low transition temperatures may not be true glass transitions. Howard and co-workers[12] tried to measure the glass transitions of copolymers made from butyl isocyanate with ethyl isocyanate using dynamic mechanical and DSC analyses. From the dynamic mechanical analyses, they found two peaks in tan δ, one in the range -20 to 0 °C and another near 100 °C. However, they could not observe the glass transition temperatures from DSC analyses and concluded that ΔC_p must be very small and therefore the DSC method could not be used to measure T_g with these alkyl isocyanate polymers. The results of our T_g analyses are given in Table V and Figure 5. In contrast to the reports of Aharoni and Howard et al., the DSC curves clearly showed the glass transition temperatures of the undecyl isocyanate copolymers.

From the dynamic mechanical analysis, Young's modulus and the loss factor (tan δ) were obtained as a function of temperature through the glass transition region. Sample results are given in Figure 6; the peak in tan δ is quite distinct. The copolymers all showed one tan δ peak in the temperature range -15 to -40 °C. The glass transition temperatures (tan δ peak) are included in Table V.

The glass transition temperatures obtained from DSC analysis and dynamic mechanical measurements were in reasonable agreement. In Figure 7 these values are plotted as a function of the number of carbon atoms (n) present in the comonomer, the homopolymer being the n = 11 member of the series.

As seen from both analyses, glass transition temperatures of these copolymers decreased first when the comonomer chain length was increased from ethyl to hexyl. After this, the glass transition temperatures increased with further increase in chain length from octyl to undecyl. This behavior may be associated with the increasing hydrocarbon content of the copolymers; this hypothesis was tested by examining reported trends in homologous series

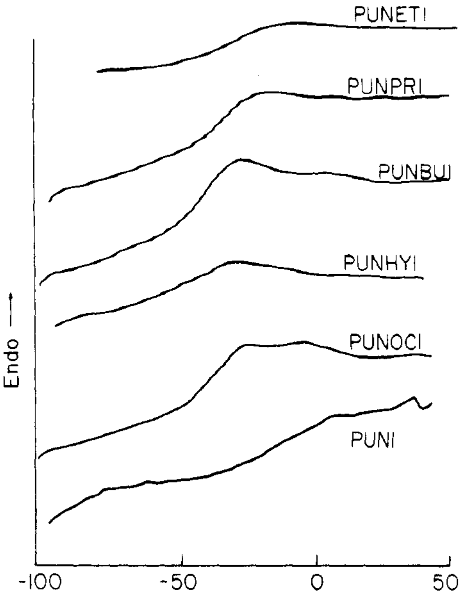

Figure 5. DSC scans for poly(undecyl isocyanate) and its copolymers showing glass transitions. Abbreviations are listed in Table I.

of alkyl-substituted homopolymers. The relevant series examined have as their $n = 1$ member the following polymers: poly(methyl chloroacrylate); polypropylene; poly(vinyl methyl ether); poly(methyl acrylate); poly(methyl methacrylate); poly(p-methylstyrene).

The T_g's for these polymers, with up to 13 methylene units in the side chain (m), were obtained from a number of sources, mainly the Polymer Handbook.[19] While the reported T_g's are not without error, the general trend with m is a decrease, followed by an increase. For application of this trend to the polyisocyanate copolymers, the entire set of T_g's was fitted to the following empirical model:

$$1 - \frac{T_g}{T_{g,0}} = m(a_1 + a_2 m + a_3 m^2 + a_4 T_{g,0})$$

with the following values for the constants

$a_1 = 0.0723 \pm 0.0199$ $\quad a_2 = -0.0126 \pm 0.0045$
$a_3 = 0.00044 \pm 0.00026$ $\quad a_4 = 0.00010 \pm 0.000047$

Note that $m = n - 1$ and $T_{g,0}$ is the T_g of the $m = 0$ ($n = 1$) member.

While this does not provide a perfect fit ($r^2 = 0.67$, $F = 32.7$), it does describe the major trends and was hypothesized to be a good predictor for the expected behavior of the T_g for poly(alkyl isocyanates). As the position of T_g of poly(undecyl isocyanate) ($m = 10$) at −15 °C was very close to that of the polyacrylates, a $T_{g,0}$ of 10 °C was assumed; this would correspond to poly(methyl isocyanate).

With this in hand the above relationship then provides the T_g's for homopolymers of $m < 10$. To predict the T_g's of 50:50 copolymers, the Fox equation was assumed. While descrepancies from the Fox equation have been described,[20] it is not evident how corrections can be made without additional information. The resulting predicted Tg's for the copolymers are depicted by the dotted line in Figure 7. It is clear from the near agreement between the data and the prediction that the known dependence of homopolymer T_g on alkyl side chain length is completely sufficient for explaining the observed minimum. This agreement also provides further support for the hypothesis that the observed transition is, indeed, the primary (glass) transition.

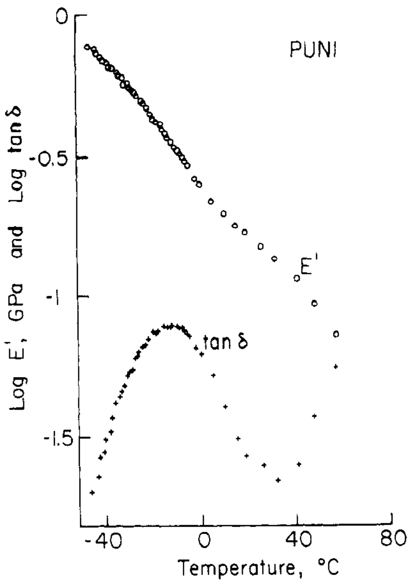

Figure 6. Dynamic mechanical analysis of poly(undecyl isocyanate), confirming glass transition at ~−10 °C.

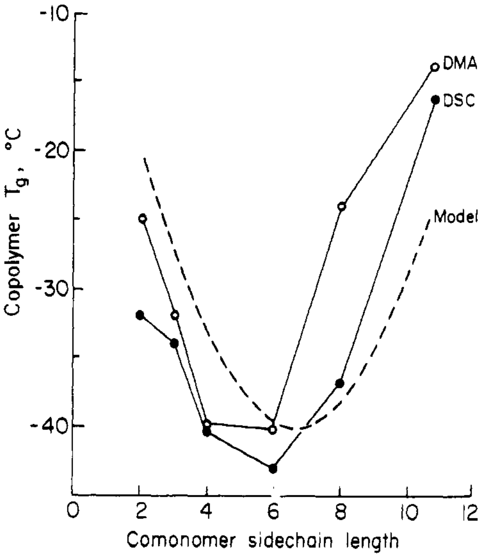

Figure 7. Summary of glass transitions for undecyl isocyanate copolymers gathered by using differential scanning calorimetry (DSC) and dynamic mechanical analysis (DMA). The broken line (model) was calculated by using T_g data for similar alkyl-substituted polymers; see text for details.

All the stress–strain curves of undecyl isocyanate copolymers showed a smooth and moderate curvature with no distinctive features. The stress–strain behavior of poly(undecyl isocyanate) was similar to that reported by Aharoni[21] for this polymer. The failure of the undecyl/hexyl copolymer occurred at a uniquely high strain. Comparing the viscosity (η_{inh}) and strain values of these copolymers indicates that the strain at failure increases with intrinsic viscosity ($p = 0.019$) but is not correlated with copolymer structure. We were unable to confirm the finding of Howard and co-workers[13] that the tensile strength and modulus are inversely dependent on the length of the side chain.

Conclusions

Liquid crystalline copolymers containing 50:50 mol ratios of undecyl isocyanate with propyl, butyl, hexyl, and octyl isocyanate were synthesized and characterized. By making copolymers, the temperature range of the isotropic state (i.e., range between the clearing and decomposition temperatures) was increased over that for poly(undecyl isocyanate). The results from various analyses showed that all the copolymers undergo decomposition at ~180 °C. The dependence of T_g on alkyl side chain length and copolymer composition was consistent with that for other alkyl side chain polymers.

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References and Notes

(1) Samulski, E. T. *Phys. Today* **1982.**
(2) Samulski, E. T. In *Liquid Crystalline Order in Polymers*; Blumstein, A., Ed.; Academic: New York, 1978.
(3) Cifferi, A.; Krigbaum, W. R.; Meyers, R. B. *Polymer Liquid Crystals*; Academic: New York, 1982.
(4) Shashoua, V. E. *J. Am. Chem. Soc.* **1959,** *81,* 3156.
(5) Shashoua, V. E.; Sweeny, W.; Tietz, R. F. *J. Am. Chem. Soc.* **1960,** *82,* 866.
(6) Aharoni, S. M. *Macromolecules* **1979,** *12,* 94.
(7) Aharoni, S. M.; Walsh, E. K. *J. Polym. Sci., Polym. Lett. Ed.* **1979,** *17,* 321.
(8) Aharoni, S. M.; Walsh, E. K. *Macromolecules* **1979,** *12,* 271.
(9) Aharoni, S. M. *Macromolecules* **1979,** *12,* 537.
(10) Aharoni, S. M. *J. Polym. Sci., Polym. Phys. Ed.* **1980,** *18,* 1303.
(11) Aharoni, S. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1980,** *21* (1), 209.
(12) Owadh, A. A.; Parsons, I. W.; Hay, J. N.; Howard, R. N. *Polymer* **1979,** *19,* 386.
(13) Ahmed, M. S.; Parsons, I. W.; Hay, J. N.; Howard, R. N. *Polymer* **1980,** *21,* 116.
(14) Boehmer, J. N. *Recl. Trav. Chim.* **1936,** *55,* 379.
(15) Durairaj, B.; Dimock, A. W.; Samulski, E. T.; Shaw, M. T. *J. Polym. Sci., Part A: Polym. Chem.* **1989,** *27,* 3211.
(16) Bur, A. J.; Fetters, L. J. *Chem. Rev.* **1976,** *76,* 727.
(17) Edgar, O. B.; Hill, R. *J. Polym. Sci.* **1952,** *8,* 1.
(18) Polmanteer, K. E.; Hunter, M. J. *J. Appl. Polym. Sci.* **1959,** *1,* 3.
(19) *Polymer Handbook*; Brandrup, J., Immergut, E. H., Eds.; John Wiley & Sons: New York, 1975.
(20) Aharoni, S. M. *Polymer* **1981,** *22,* 418.
(21) Johnson, N. W. *J. Macromol. Sci., Rev. Macromol. Chem.* **1976,** *C14,* 215.

Registry No. PUNI, 68664-35-7; PUNETI, 124605-39-6; PUNPRI, 104474-24-0; PUNBUI, 104475-25-1; PUNHYI, 104474-26-2; PUNOCI, 104474-27-3.

Synthesis of Nonionic Hydrogel, Lipogel, and Amphigel by Copolymerization of 2-Oxazolines and a Bisoxazoline[1]

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ABSTRACT: As a novel method for the preparation of a hydrogel based on a polyoxazoline, the copolymerization of 2-methyl-2-oxazoline and 2,2′-tetramethylenebis(2-oxazoline) was carried out with methyl triflate initiator. The obtained gel was isolated almost quantitatively after Soxhlet extraction. The resulting hydrogel showed a high swelling degree both in water and in 5% aqueous sodium chloride. The water uptake was up to 45 multiples of the weight of the dry gel. 2-Oxazoline monomers with various 2-alkyl substituents (methyl, ethyl, *n*-propyl, *n*-butyl, and *n*-octyl) were also copolymerized with the above bisoxazoline to produce gels having a wide variety of swelling characteristics, i.e., from hydrogel to lipogel (organogel) depending on the substituents. The gels from 2-*n*-propyl- or higher alkyl-2-oxazoline showed the characteristic properties of lipogels and were swollen in less polar organic solvents such as toluene or 1,2-dichloroethane. The gel from 2-ethyl-2-oxazoline was a characteristic amphiphilic gel (amphigel), which was swollen both in water and in organic solvents.

Introduction

Hydrogels are known to be one of the most interesting polymeric materials, especially in various fields such as household articles, horticulture, coating materials, and civil engineering. Most hydrogels investigated so far have ionic groups such as carboxylic acids and sulfonic acid salts as the hydrophilic group. Recently, explorations of methods for the preparation of nonionic hydrogels have been reported[2-6] more and more.

Very recently, we reported a novel nonionic hydrogel starting from 2-methyl-2-oxazoline as shown in Scheme I.[7] Generally, poly(2-methyl-2-oxazoline) has unique properties such as high hydrophilicity and good compatibility with several organic polymers.[8] We also demonstrated the partial hydrolysis of poly(2-methyl-2-oxazoline) followed by a cross-linking reaction to give a

Scheme I