Synthesis and Molecular Composites of Functionalized Polyisocyanates[1]

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ABSTRACT: Side chain functionalized polyisocyanates with ether, ester, and ketone groups, i.e. poly(3-(benzyloxy)-*n*-propyl isocyanate) (PIET), poly(3-(benzyloxycarbonyl)-*n*-propyl isocyanate) (PIES), and poly(3-oxobutyl isocyanate) (PIK), were synthesized to enhance the possibility of forming miscible blends with hydrogen-bonding donor random coil polymers. While such blends do not form with poly(*n*-hexyl isocyanate) (PHIC) and a 91/9 copolymer of styrene and vinylphenol (PHS-9), several criteria are consistent with miscible blend formation with the functionalized polyisocyanates above. Infrared spectrometry demonstrates hydrogen bonding between the phenol hydroxyl groups and the polar side chain functions. The glass transitions of the blends are intermediate between those of PHS-9 and the polyisocyanate in certain composition ranges in which optical microscopy shows no evidence of birefringence or cloudiness. Optical activity properties and light-scattering measurements show that PIES and PIET are stiff helical macromolecules, as is well-known for PHIC. PIES was hydrogenolyzed to yield the unprotected polymer with carboxylic acid pendant groups. This polyelectrolyte was soluble in water with a pH 7 buffer and at higher pH's but with a depolymerization whose rate increased at higher pH.

Introduction

There is a conflict between the desire to enhance the mechanical properties of coil-like polymers by forming molecular composites with rigid polymers[2] and the inherent barrier associated with forming a single phase of mixtures of high molecular weight polymers of any type of dimensional characteristic.[2] The key to miscibility, as analyzed by Flory,[3] is to gain a negative free energy of interaction between the polymers to overcome the fact that "The entropy to be gained by intermixing of polymer molecules is very small owing to the small numbers of molecules involved".[3] Many[4] have followed Flory's suggestion to use polar interactions to achieve the goal of miscibility.

In the situation of attaining miscibility of coil and stiff polymers, the propensity of the latter to form liquid crystal regimes which exclude the coil polymers adds an extra burden to miscibility.[5] Nevertheless, using polar interactions, including the prominent use of hydrogen bonding, many examples of such blends exist.[6]

The stiff helical polyisocyanates[7] because of the ratio of their persistence length to their diameter and also because of the side chain variability have been suggested as desirable components of molecular composites.[8,9] In one attempt though to polymerize a solution of PHIC dissolved in styrene, phase separation occurred even though the original solution was isotropic.[10] In this experiment there is no polar interaction between the stiff and random coil polymers. PHIC does though have a hydrogen-bonding acceptor group in the backbone. We therefore attempted to improve on this by blending, from a dilute solution, PHIC with a copolymer of 91% styrene and 9% vinylphenol (PHS-9) but still observed phase separation by various criteria.

As discussed in detail below, we therefore synthesized three polyisocyanates with hydrogen-bonding acceptor groups in the side chains. In each case we form blends with PHS-9 via the formation of hydrogen-bonding interactions between the phenolic hydroxyl group and the side chain acceptor group, as judged by infrared studies. These blends, over wide composition ranges, pass the test of miscibility at least as judged by the criteria of microscopy and differential scanning calorimetry (DSC). The blends are exceptional in allowing up to equal weight percentages of the polyisocyanates and PHS-9 without evidence of phase separation up to the decomposition exotherm near 200 °C.

Results

Synthesis and Properties of Side Chain Functionalized Polyisocyanates. In an attempt to prepare a molecular composite based on the polyisocyanates, we prepared a copolymer of 9% acetoxystyrene with 91% styrene which was then hydrolyzed to the vinylphenol−styrene copolymer (PHS-9).[11] The idea was to gain a miscibilizing hydrogen bond between the coil and the recurring amide group in the PHIC backbone. The polymers formed a clear film on casting from tetrahydrofuran, but DSC measurements on films which had been heated to 140 °C and quenched showed the glass transition temperature, T_g, to be the same as for PHS-9. PHIC is known to have a T_g well below room temperature.[12]

To enhance the hydrogen-bonding interaction between the polyisocyanate and PHS-9, we synthesized several polyisocyanates with hydrogen bond acceptor groups in the side chains. Scheme 1 shows the preparation of the monomers.

The monomers M−1 to M−3 were polymerized in toluene at −78 °C initiated by sodium cyanide in dimethylformamide[13] to obtain the corresponding side chain functionalized polyisocyanates PIK, PIET, and PIES (Chart 1). The structure of PHS-9 is also shown.

The polymerization of functionalized isocyanate monomers has been recently reported using organometallic initiators.[14] Following this we attempted the polymerization of all three monomers in Scheme 1 using the reported titanium complex $CpTiCl_2(OCH_2CF_3)$ (Cp = cyclopentadienyl). We were only successful in obtaining polymer from monomer M−1. This material, PIET, was identical in its structure to that formed by the sodium

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Scheme 1

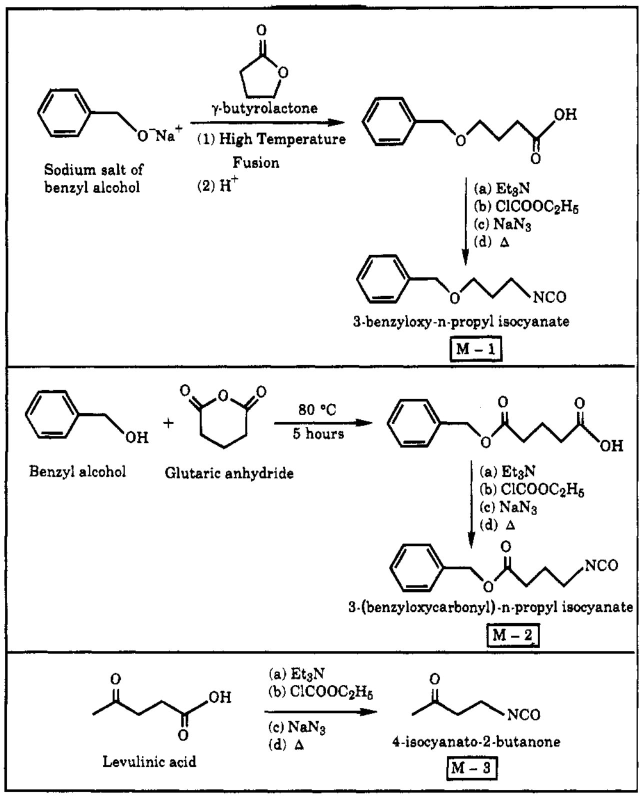
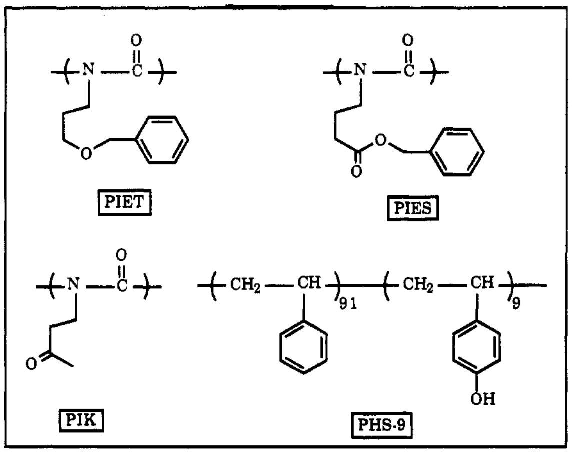


Chart 1



cyanide method.[13] The potential enolate in monomers M−2 and M−3 may preclude its polymerization using the titanium complex.[15]

The monomers in Scheme 1 were also designed to take advantage of potential chemical side chain transformations to form hydrogen-bonding interactions as donors, broadening the blending potential and even the potential for forming water soluble polyisocyanates. In the case of PIET and PIES replacement of the benzyl group by hydrogen, which classically is carried out by hydrogenolysis,[16] would accomplish this objective, while in PIK, the transformation would require reduction of the ketone group. In this way PIET, PIES, and PIK might be converted to polyisocyanates with carboxylic acid and hydroxyl side chain functionalized groups.

Control experiments were carried out in which benzyl hexyl ether and benzyl propionate were separately subjected to hydrogenolysis in tetrahydrofuran (THF) on palladium on charcoal (Pd/C) in the presence of PHIC. The hydrogenolysis occurred readily to yield the derived alcohol and carboxylic acid, respectively, without degrading the PHIC, as judged by infrared spectra and viscosity measurements.

In the case of PIK, use of hydrogenation on a nickel catalyst modified with optically active tartaric acid[17,18] could yield the enantiomerically enriched hydroxyl-bearing polyisocyanate in one step. Although we found PHIC to be stable to these conditions in an appropriate solvent for this process, i.e. THF, unfortunately PIK was not soluble in this solvent. The use of the alternate solvent dimethylaetamide caused depolymerization of PIK to trimer. This may occur following the formation of dimethylamine which is known to depolymerize polyisocyanates.[19] In principle the ketone functionality could also be reduced to the hydroxy group by using lithium aluminum hydride or sodium borohydride but unfortunately we found that these reagents also decompose PHIC to trimer. Other attempts were not made using the wide range of reducing agents available for conversion of ketones to alcohols.

Cleavage of a benzyl group using large pore size Pd/C as a catalyst to prepare poly(methacrylic acid), poly(acrylic acid), and poly(malic acid) from the respective benzyl esters is known.[20] Hydrogenolysis of the benzyl ester group from poly(benzyl L-glutamate) also occurs under these conditions, but in the case of this stiff polymer the process is more sensitive to molecular weight.[21] This is considered to arise from the steric restrictions associated with fitting the stiff polymer into the active sites of the palladium.[20]

Use of Pd/C catalyst of the generally used Degussa type in several solvents either gave no cleavage of the benzyl group in PIES or poor cleavage in several solvents. Use of Johnson-Matthey specially prepared large pore size Pd/C catalyst for the hydrogenolyses of PIET and PIES in THF still caused no cleavage of the benzyl group. When the solvent medium of the reaction was changed to dimethylacetamide (DMAc) in the large pore size catalyst, a complete cleavage of the benzyl group from a low molecular weight sample of PIES to yield poly(isocyanatobutyric acid) (PBAIC) took place. For a higher molecular weight sample of PIES the process was retarded, and as shown by carbon NMR only a partial cleavage of the benzyl group was observed. Under similar conditions cleavage of the benzyl group from PIET of a lower molecular weight than that necessary for successful cleavage of PIES did not take place. It is well-known that benzyl ethers are more difficult to hydrogenolyze than benzyl esters.[16]

The poly(carboxylic acid), PBAIC, which was produced by the successful hydrogenolysis discussed above was characterized by carbon and proton NMR and by infrared spectrometry and was found to be soluble only in highly polar solvents but not in neutral water. It does dissolve though in pH 7 buffer and at higher pH's, but with decomposition to the isocyanurate trimer. This decomposition which was followed by carbon NMR was more rapid at pH 9.5 than at pH 7. In the latter case the process took several days.

Although the conformational and dimensional characteristics of PHIC are precisely defined,[7,22] there has been little study on the role of functionalized side chains on these properties.[23] Recently, polyisocyanates have been synthesized with a variety of alkoxymethyl side chains and light-scattering studies on a model of this class show a coil-like property distinct from the stiff characteristics of the poly(alkyl isocyanates).[24] In this polymer[24] a single methylene group intervenes between

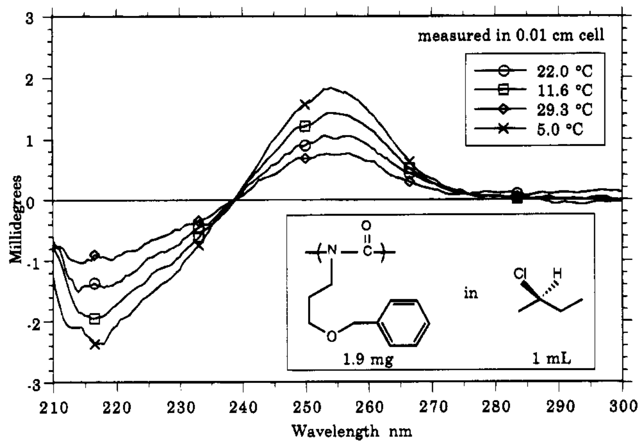


Figure 1. Circular dichroism spectra of PIET in (*R*)-2-chlorobutane as a function of temperature.

the oxygen and the backbone, as is the situation in an azo-substituted polyisocyanate[25] where copolymerization properties and UV spectra suggest differences in conformational properties from the poly(alkyl isocyanates). In the latter study the intervention of a three methylene group spacer to the azo function acts to insulate the side chain function, as judged by these properties. This effect parallels that in the polyisocyanates discussed herein since light-scattering studies show that PIES has nearly the same dimensional properties as PHIC in methylene chloride.[26] In PIK, where the carbonyl group is spaced only two methylene groups from the backbone, these same studies show a reduction in persistence length, although not to the level found with the side chain studied by Wudl and coworkers.[24]

There is though one fascinating difference in the properties of both PIET and PIES from PHIC in the effect of solvent on the dimensional properties. In PHIC it has been long known that polar solvents cause a reduction in viscosity and for that matter in persistence length as well.[27] This has been connected to changes in local segmental motion affected by dipolar interactions with the solvent.[28] For unknown reasons PIES acts in the opposite manner compared to PHIC. While the persistence length of PIES in 22 nm in dichloromethane it is reduced to 15 nm in toluene based on viscosity and light-scattering studies.[26] Moreover an optically active copolyisocyanate synthesized by polymerizing 94 mol % of M-2 and 6 mol % of (*R*)-2,6-dimethylheptyl isocyanate had an optical rotation value at 365 nm of −790° in dichloromethane and −660° in toluene. In the optically active poly(alkyl isocyanates) the opposite is observed with lower optical activities in polar solvents.[7]

The question still remains as to the conformational details of the backbone in the polyisocyanates under study here. In PHIC this is well-known to be helical with unusual sensitivity to chiral effects arising from the difficulty in introducing helix reversals in the chain.[7] This characteristic manifests itself in several ways including an induction of an excess helical sense along the backbone by simply dissolving PHIC in optically active solvents. Such an effect is called a first-order asymmetric transformation.[29] This observation and especially its temperature dependence,[29] which may be considered a signature of the local helical stiff conformational properties, is also seen in PIET, as shown in Figure 1. Moreover comparison of the intensities of the CD bands in Figure 1 against those for PHIC of the same degree of polymerization and concentration[29] show them to be almost identical, demonstrating comparable levels of cooperativity and therefore backbone structure. The UV spectrum of PIET in 2-chlorobutane exhibited a λ_{max} near 250 nm with an extinction coefficient of 3750 L mol^{-1} cm^{-1}. For PIES in THF, the λ_{max} was near 252 nm and the extinction coefficient was 4500 L mol^{-1} cm^{-1}. This slight blue shift in the chlorinated solvent is also observed for PHIC. The extinction coefficient though for this band in PHIC in chloroform is 4200 L mol^{-1} cm^{-1}. In polyisocyanates where the UV and CD band wavelengths are known to be sensitive to the conformational properties of the backbone,[30] the CD pattern seen in Figure 1 for PIET, which is identical to that for PHIC, further emphasizes the comparable local conformational properties in these polymers.

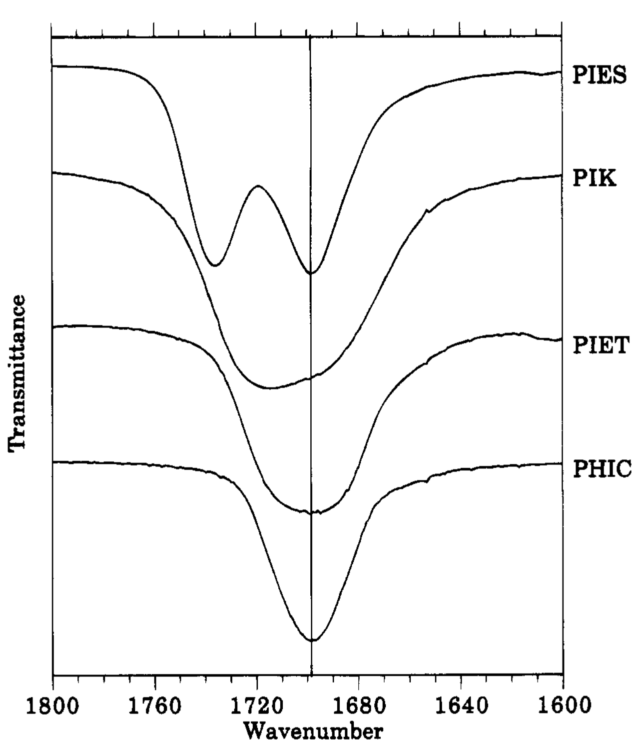


Figure 2. Comparison of the backbone carbonyl frequency of PHIC with functionalized polyisocyanates.

Infrared spectra were obtained for the three functionalized polyisocyanates PIET, PIES, and PIK, and the frequency of the carbonyl peak of the backbone was found to be at 1700 cm^{-1}, which is the same as in PHIC and supports the above conclusion as to the absence of interaction between the functional group in the side chain and the isocyanate backbone. These data are shown in Figure 2. Moreover the position of the backbone carbonyl in the ^{13}C NMR spectra is near 156 ppm in all the three polymers in $CDCl_3$ which is also true for PHIC in this solvent. In the work with a single methylene group separating the etherial oxygen from the backbone the position of the backbone carbonyl is reported to be at 1740 cm^{-1}.[24] This shift of the carbonyl frequency from the normally observed 1700 cm^{-1} may be related to the more flexible properties reported for this polymer.[24]

Attempted Formation of Molecular Composites from Functionalized Polyisocyanates. Since methylene chloride dissolves all three side chain functionalized polyisocyanates as well as PHS-9, we made 2.5 weight % solutions of various compositions of each of the polyisocyanates with PHS-9 in this solvent and cast

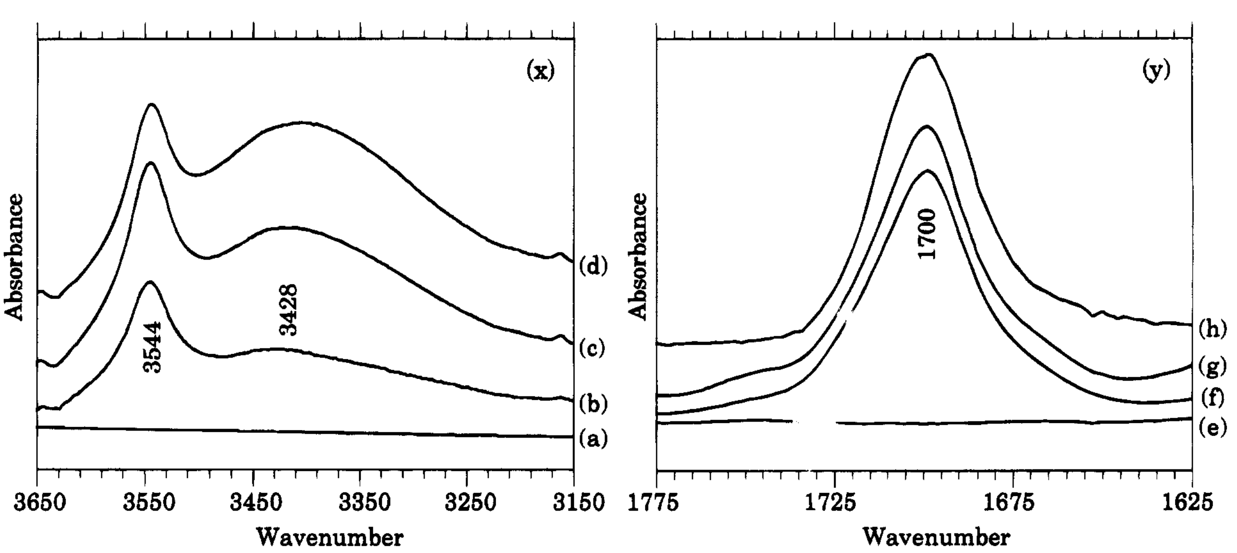


Figure 3. (x) (a) PIET, (b) PHS-9, (c) PHS9/PIET (90/10), (d) PHS-9PIET (80/20). (y) (e) PHS-9, (f) PHS-9/PIET (80/20), (g) PHS-9/PIET (90/10), (h) PIET.

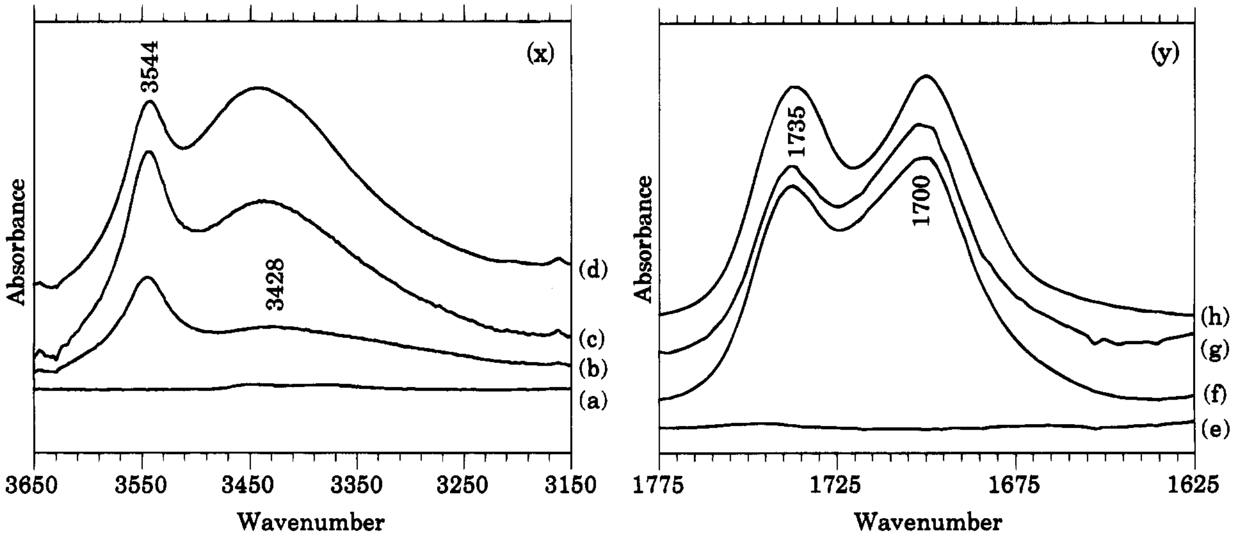


Figure 4. (x) (a) PIES, (b) PHS-9, (c) PHS-9/PIES (90/10), (d) PHS/PIES (80/20). (y) (e) PHS-9, (f) PHS-9/PIES (80/20), (g) PHS-9/PIES (90/10), (h) PIES.

films by slow evaporation. These films were subjected to analysis by infrared spectrometry in the hydroxyl and carbonyl regions of the spectrum which are shown for various compositions (Figures 3–5) for PIET, PIES, and PIK, respectively.

Analyses of the infrared spectra in the carbonyl region indicate that the backbone carbonyl remains at 1700 cm^{-1}, while the side chain carbonyl groups in both PIES and PIK lose intensity as PHS-9 is added. This behavior has been observed for the methyl and ethyl esters of poly(L-glutamic acid) when blended with poly(vinylphenol)[31] where the intensity of the side chain ester carbonyl of the polypeptide which appears at 1735 cm^{-1} decreases and a new peak at 1715 cm^{-1} corresponding to the hydrogen-bonded carbonyl is observed in the blends. This parallel situation here leads to the conclusion that the side chain carbonyl in PIES and PIK is shifted in part to lower frequencies, but it is difficult to resolve the bonded carbonyl, which appears at 1715 cm^{-1}, from the main chain carbonyl. In PIET which has no carbonyl group other than that in the backbone, the carbonyl band is unaffected by PHS-9, suggesting the source of the hydrogen bond forming interaction arises from the side chain.

A possible cause for the carbonyl side chain to lose its intensity as discussed above is hydrogen bonding to the phenolic hydroxyl group in PHS-9. This is nicely supported by the infrared data in the hydroxyl region in Figures 3x, 4x, and 5x. While the spectral data for PHS-9 show only small proportions of hydrogen-bonded hydroxyl at 3428 cm^{-1} compared to free hydroxyl at 3544 cm^{-1}, blending with PIET, PIES, or PIK leads to shifts of spectral intensity to the lower frequency band. Since we see in PIET that the backbone carbonyl is unaffected by the presence of PHS-9, we must conclude that the side chain carbonyl is the hydrogen-bonding partner consistent with the infrared data in the carbonyl region. The infrared results suggest an intimate spatial relationship between the side chain functionalized polyisocyanates and PHS-9.[32]

The blend samples with low polyisocyanate content are transparent when viewed by phase contrast optical microscopy at room temperature and do not show any birefringence under crossed polars. Several samples were studied at 140 °C, a temperature that was obtained by heating at 20 °C/min. Under these conditions we observe phase-separated material as evidenced by immediate cloudiness when the polyisocyanates' composi-

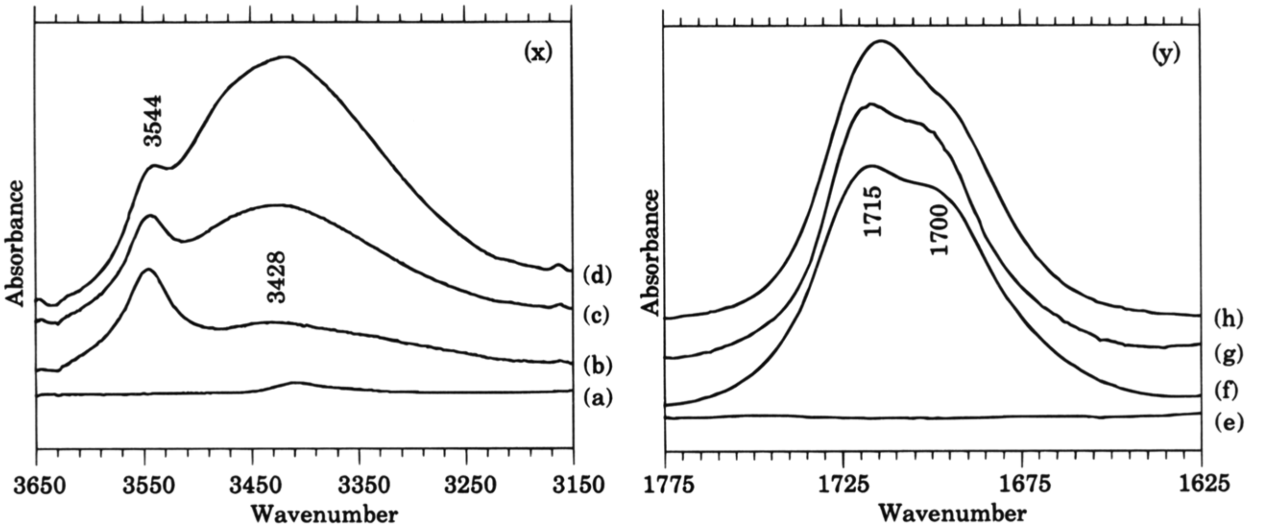


Figure 5. (x) (a) PIK, (b) PHS-9, (c) PHS-9/PIK (90/10), (d) PHS-9/PIK (80/20). (y) (e) PHA-9, (f) PHS-9/PIK (80/20), (g) PHS-9/PIK (90/10), (h) PIK.

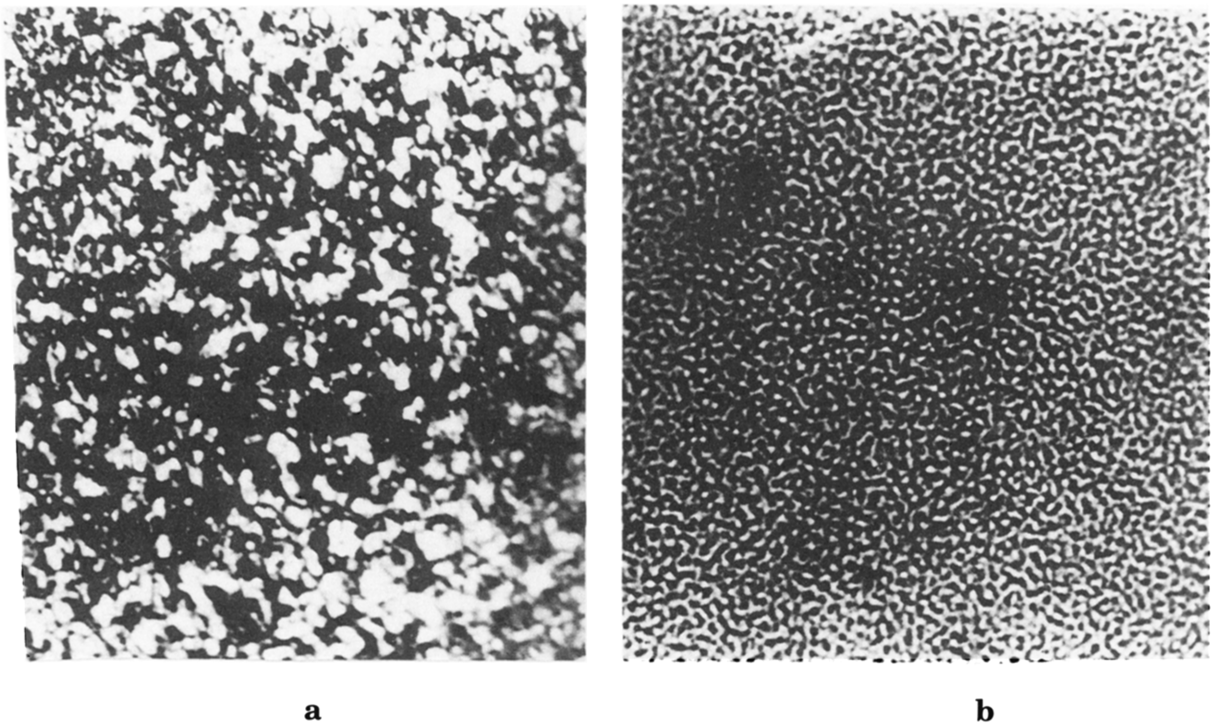

a
b

Figure 6. Optical micrographs of PIES/PHS9 (75/25): (a) texture observed under cross-polar at room temperature; (b) texture observed through phase contrast microscopy at 140 °C.

tions are over 50% in PIES and in PIET, and over 25% in the PIK blends. At lower compositions of the polyisocyanate no evidence for phase separation in terms of cloud points was observed when the samples were heated to 200 °C. At these high temperatures we expect decomposition to occur.

The PIES samples with more than 50% of the stiff component show birefringence at room temperature. The texture of the pattern as shown in Figure 6 is typical for nematic phases.[33] The investigated blend samples in this composition region, i.e. above 50% of the PIES, lose the birefringence at temperatures about 140 °C, above which the samples are isotropic under crossed polars. The formation of the birefringence was not reversible, the samples remained isotropic under crossed polars after cooling back to room temperature. Phase contrast microscopy shows though that these samples are still phase separated. Presumably, the polymer dynamics do not permit the reorganization necessary to form the birefringence character in the polyisocyanate phase as the temperature is lowered. PIET and PIK blends showd no birefringence after solvent casting, presumably also due to restrictions in polymer dynamics.

Interestingly, these samples with high PIES content show phase-separated cocontinuous patterns typical for spinodal decomposition[34] (Figure 6b) when viewed by phase contrast microscopy at 140 °C. At temperatures below the PIES melting (see below, Figure 10) the birefringence interferes with observation of the spinodal from the phase-separated domains although presumably it may be still present. Presently, we are investigating the connection between the phase separation and the formation of the anisotropic structures with regard to the precise phase boundaries which will be determined in further studies.

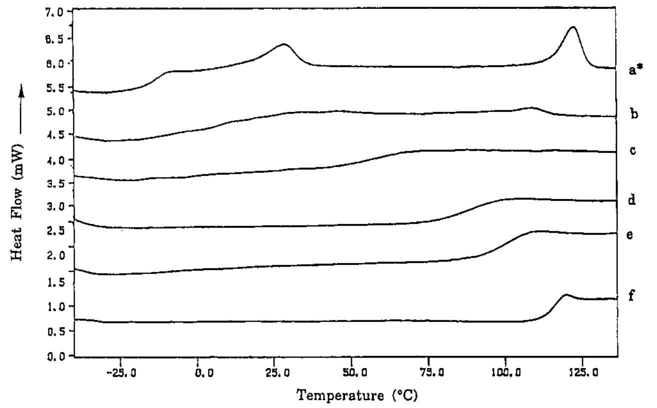


Figure 7. Differential scanning calorimetry of PIET PHS-9, and their blends: (a) PIET, (b) PIET/PHS-9 (75/25), (c) PIET/PHS-9 (40/60), (d) PIET/PHS-9 (20/80), (e) PIET/PHS-9 (10/90), (f) PHS-9. *Multiply by 3 mW to compare it with other thermograms.

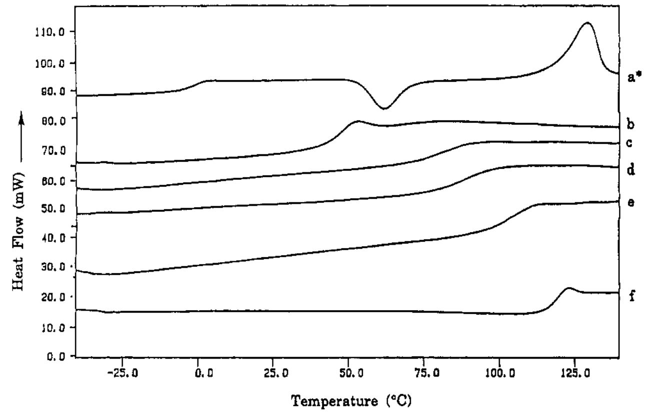


Figure 8. Differential scanning calorimetry of PIES, PHS-9, and their blends: (a) PIES, (b) PIES/PHS-9 (50/50), (c) PIES/PHS-9 (25/75), (d) PIES/PHS-9 (20/80), (e) PIES/PHS-9 (10/90), (f) PHS-9. *Multiply by 17.14 mW to compare it with other thermograms.

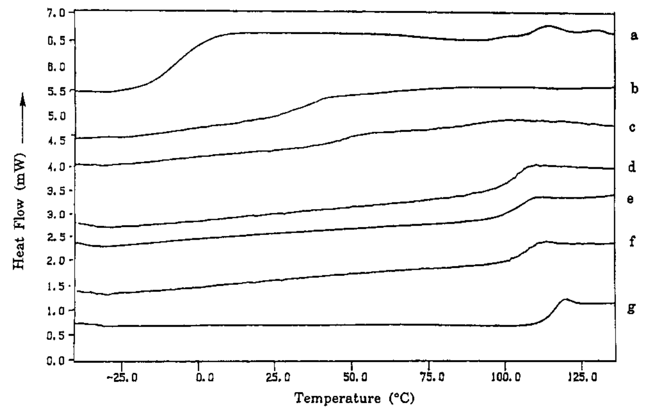


Figure 9. Differential scanning calorimetry of PIK, PHS-9, and their blends: (a) PIK, (b) PIK/PHS-9 (90/10), (c) PIK/PHS-9 (60/40), (d) PIK/PHS-9 (25/75), (e) PIK/PHS-9 (20/80), (f) PIK/PHS-9 (10/90), (g) PHS-9.

The DSC results in Figures 7–9 offer no resistance to the conclusion of miscibility in the low stiff chain composition regions. In contrast to poly(alkyl isocyanates) where the glass transition temperature, T_g, is difficult to resolve,[12] this parameter is readily seen in the pure samples of PIET, PIES, and PIK, as is also seen in the large shift to an intermediate single T_g occurring in the blends of these polyisocyanates with PHS-9 (Figures 7–9). Moreover, in homogeneous samples of PIET and PIES which show thermal transitions associated with orderd states, these transitions are absent in the blends.

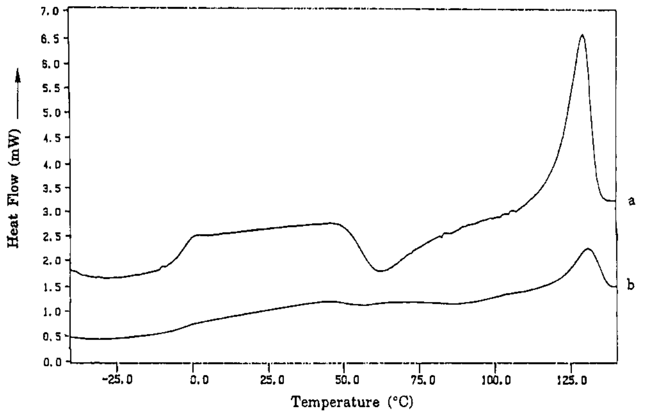


Figure 10. Differential scanning calorimetry of PIES and PHS-9 blend with high PIES contents: (a) PIES/PHS-9 (90/10), (b) PIES/PHS-9 (75/25).

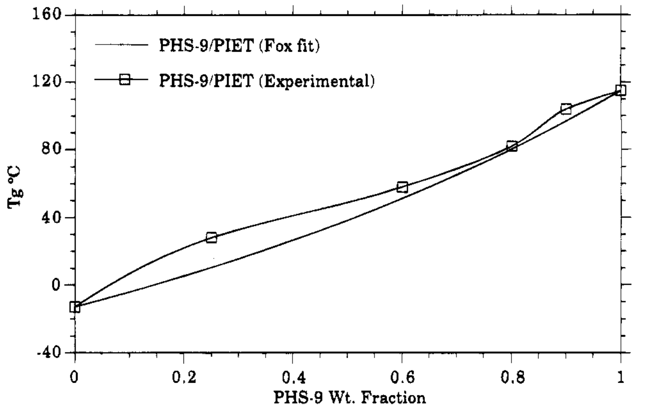


Figure 11. Theoretical dependence of the glass transition temperature of PHS-9/PIET blends using the Fox equation.

Pure PIES shows exothermic order formation and endothermic melting, as shown in Figure 10. The blend samples with 90 and 75% PIES show the same exothermic and endothermic transitions. These samples were birefringent. In the blends with 50% PIES or less these transitions are not seen and only a single T_g is observed (Figure 8). The behaviors of PIET blends are very similar: a single glass transition is observed up to 50% of PIET and the higher compositions are phase separated.

The glass transitions of the blends with 25% or less of the PIK component are clearly lower than the T_g value of PHS-9. These samples were indicated to be homogeneous by the infrared and optical studies also. The sample with 50% PIK (and higher PIK compositions) are phase separated at 140 °C. The same solvent cast samples show cloudiness.

Figures 11 and 12 show the experimental composition dependence of the glass transition behavior of PHS-9/PIET and PHS-9/PIES blends, respectively, and are compared with glass transition temperatures theoretically obtained using the Fox equation.[35] For PHS-9/PIES and PHS-9/PIET blends the experimental T_g's fit the Fox equation well in the miscible composition region.

Discussion

In the work above a miscible state in certain blend compositions was indicated by a single glass transition behavior, by infrared evidence for interaction, and by

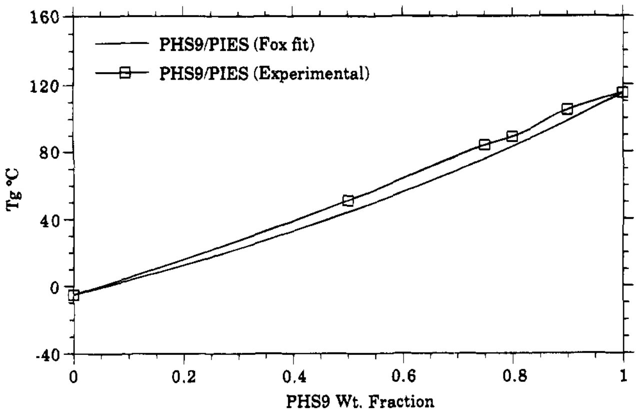


Figure 12. Theoretical dependence of the glass transition temperature of PHS-9/PIES blends using the Fox equation.

optical clarity. The resolution of these methods has limitations. For example in our phase-separated samples no birefringence was observed, presumably due to the restrictions in polymer diffusion, but DSC analysis did show endothermic melting. This is evidence for DSC analysis being more accurate than optical studies. In the regions where there are low compositions of the stiff component, the amount of ordering of the stiff polymer may be too low to be detected by DSC measurements.[36]

The polyisocyanates are now the second example of a class of stiff polymers subjected to blending studies which exhibit optical activity in solution.[31] In dilute solution the light samples on isotropic array of the stiff macromolecules and this number therefore could be interesting to compare to the optical activity in the blended state as a test of the isotropic arrangement. If the chiral component is oriented with respect to the impinging light, the optical activity can be expected to differ from that in isotropic solution.[37]

Such a measurement offers no difficulty since this property can be measured far from the absorption bands in the visible region of the spectrum. In addition, control experiments on solvent cast films of blends of PIES with PHS-9 show no optical activity, indicating the absence of form birefringence;[38] i.e. the blend behaves as a solid solution. We have taken this opportunity to measure the optical activity in the blend in the preparation of an optically active sergeants and soldiers copolymer[39] of 94% M-2 units with 6% (*R*)-2,6-dimethylheptyl isocyanate units. When this copolymer is blended with PHS-9 in a composition of 70/30 under the conditions discussed above, and a thin film is cast from solution, both the D line and 365 nm specific rotations, calculated by knowledge of the film thickness and the composition, are found to be smaller by about a factor of 4 compared to the values in dilute solution in toluene. Work is in progress to adapt the polarimeter equipment to measure optical activities in blends with far smaller proportions of the copolyisocyanate to judge the effect of concentration on this comparison. It would be interesting to make parallel measurements on the blended polypeptides.[31]

We have also varied the temperature of this film of the optically active blend and observed no change in optical activity below the region of the glass transition, the latter independently determined by DSC measurements. This experiment is consistent with the known necessity[7,39,40] for a change in population of the helix reversals as a prerequisite to a change in the optical activity. The helix reversals form a kink in the otherwise stiff chain[7] which may therefore be expected to be immobile in the glassy state. This novel detection of the glass transition[41] opens up very interesting possibilities for future study of the properties of blends composed of optically active polyisocyanates, or for that matter other optically active blend components in which the optical activity depends on conformation.

Conclusions

Polyisocyanates with ether, ester, and ketone functionalities in the side chains were synthesized. In PIES and PIET where the functional group is located three methylene groups away from the backbone the polymers appear to share the stiff helical properties associated with the poly(alkyl isocyanates). Hydrogenolysis of PIES yielded a polyisocyanate with a carboxylic acid pendant group. The PBAIC obtained in this way was soluble in highly polar solvents but not in neutral water. It dissolved though in aqueous buffers of pH 7.0 and 9.5 in which the polyisocyanate decomposed to a cyclic trimer. The rate of formation of this trimer was faster at the higher pH.

Use of DSC, infrared spectroscopy, and optical microscopy were consistent with the conclusion that the functionalized polyisocyanates formed thermodynamically stable blends with a copolymer of 91 mol % styrene and 9 mol % *p*-hydroxystyrene. Such blends, as judged by these criteria, did not form with PHIC. Infrared spectroscopy demonstrates that the hydrogen-bonding interaction is between the side chain functional groups of the polyisocyanates and the phenolic hydroxyl group of the coil-like polymer.

Experimental Section

Routine infrared spectra were recorded on a Shimadzu IR-435 spectrometer or on a Perkin-Elmer 1600 series FTIR. A JEOL FX-90Q spectrometer or a General Electric GN300 spectrometer, respectively, was used for NMR measurements. Elemental analyses were carried out by the analytical department, Institute of Macromolecular Chemistry, Academy of Sciences, CR, Prague. Viscosities were measured on a single-bulb Cannon-Ubbelohde type viscometer uncorrected for shear with flow times greater than 100 s except for chloroform where above 80 s was used. Polarimeter measurements were made on a Perkin-Elmer 141 spectropolarimeter using a 1-dm jacketed cell. CD measurements were made on JASCO 710 spectrophotometer using a 0.01 cm cylindrical quartz cell. Temperature-controlled scans were performed using a thermostated cell holder attached to a Neslab constant temperature thermostat.

The blend solution was prepared by mixing appropriate amounts of both the random coil and stiff polymers and making a 2.5 wt % solution of the mixture in methylene chloride. The solution was stirred for 14 h and poured into an aluminum pan kept in a vacuum oven set at 40 °C. Most of the solvent was first removed carefully under house vacuum, and then the sample was dried under high vacuum for 12 h at the same temperature. The samples obtained in this way was used for the DSC and hot-stage microscopy experiments. For the blend studies, the intrinsic viscosities of the PIES and PIET used were 1.69 and 2.16 dL/g in toluene at 25 °C, respectively. The absolute molecular weights of these same samples of PIES and PIET as determined from low-angle light scattering were 300 000 and 230 000, respectively.[26] The PIK used had an intrinsic viscosity in chloroform at 25 °C of 0.25 dL/g. PHS9 had molecular weight of 24 000, as determined from GPC calibrated against the polystyrene standard samples.

The DSC measurements were carried out on a Perkin-Elmer DSC7 under a nitrogen atmosphere using 5−7 mg of the sample at a rate of 20 °C/min between −60 and 140 °C. The DSC thermograms reported here are for the second heat cycle. To avoid decomposition the sample on reaching 140 °C was immediately quenched. Optical polarizing microscopy was performed using a Nickon HFX IT optical microscope equipped with a Mettler hot stage. The birefringence structures were observed between cross-polars in transmitted light and the liquid–liquid phase separation in modulation contrast mode with a Hoffman Modulation Contrast Unit.

For the blend study, infrared spectra were recorded on a Perkin-Elmer 1600 series FTIR with 2 cm^{-1} resolution under nitrogen atmosphere with a minimum of 128 scans on an as cast film of the blend or of the homopolymer from a methylene chloride solution cast on a KBr disk.

All solvents used for physical measurements were obtained either from Aldrich Chemical Co. or from Fisher Scientific. 1,2-Dichloromethane was distilled over CaH_2, dimethylacetamide (DMAc) was distilled under reduced pressure over barium oxide, THF was distilled from Na/benzophenone, and all were distilled directly before each use. DMF was distilled from P_2O_5 under reduced pressure, and toluene and xylene were distilled over sodium.

Synthetic Procedures. (Benzyloxy)butyric Acid (1). The procedure followed that of Sudo et al.[42] To 10 g of Na (0.435 mol) in 150 mL of toluene/xylene (1:1) was added 50 g of benzyl alcohol (0.462 mol) (used as received from Aldrich Chemical Co.) in 75 mL of toluene dropwise under an inert atmosphere. The mixture was refluxed to complete the reaction. γ-Butyrolactone (40 g 0.464 mol) (used as received from Aldrich Chemical Co.) was then added and the mixture was gradually heated to 225 °C. During this time the solvent evaporated, and the residue was fused at this temperature for 30 min. After cooling, the residue was dissolved in 100 mL of water and subjected to continuous extraction over ether for 2 days. The aqueous layer was acidified with dilute HCl. Continuous extraction using ether was performed to remove the oily layer. The ether extract was dried over anhydrous sodium sulfate and filtered, and solvent was removed on a rotoevaporator. The residue was distilled under reduced pressure (0.5 mmHg) to give 29.7 g of straw-colored liquid (**1**), bp 135 °C. ^{1}H NMR (TMS at 0.00 ppm) δ 1.93 (pentate, 2H), 2.46 (t, 2H), 3.51 (t, 2H), 4.49 (s, 2H), 7.31 (m, 5H), 11.25 (br, 1H); ^{13}C NMR ($CDCl_3$ at 77.00 ppm): δ 24.74, 30.93, 68.98, 72.86, 127.59, 128.37, 138.20, 179.75. The infrared spectral data were consistent with the structure.

3-(Benzyloxy)-*n*-propyl Isocyanate (2). The isocyanate was synthesized by the Curtius rearrangement of the acyl azide following the method of Kaiser and Weinstock.[43] To 11.1 g (0.057 mol) of **1** in a dry flask was added 30 mL of acetone and 9.75 mL of triethylamine (0.07 mol) (distilled over CaH_2). The mixture was stirred and cooled to 5 °C. Ethyl chloroformate (6.5 mL, 0.068 mol) was added dropwise with virgorous stirring while the temperature was maintained below 5 °C. Sodium azide (6.5 g, 0.1 mol) in 25 mL of distilled water was then added with stirring and still maintaining the temperature below 5 °C. After complete addition of sodium azide the reaction mixture was stirred for 45 min before extracting with 4 × 75 mL of ice cold toluene. The combined toluene extract was stirred over anhydrous $MgSO_4$ at low temperature and then filtered. The filtered acyl azide solution in toluene was heated gradually under an inert atmosphere to 70 °C for 30 min to perform the Curtius rearrangement. The toluene was removed under reduced pressure (12 mmHg) and the residue distilled at 0.05 mmHg to collect 5.7 g of **2** with bp 79 °C. Anal. Calcd: C, 69.02; H, 6.79; N, 7.32. Found: C, 69.04; H, 6.78; N, 7.21. ^{1}H NMR (TMS at 0.00 ppm): δ 1.87 (pentad, 2H), 3.43 (t, 2H), 3.55 (t, 2H), 4.50 (s, 2H), 7.33 (m, 5H). ^{13}C NMR ($CDCl_3$ at 77.00 ppm): δ 31.29, 40.05, 66.54, 73.15, 122.23, 129.15, 138.31. Infrared (neat): 4057, 3688 (vw, br), 3088, 3065, 3031 (w, shp), 2958, 2927, 2861 (m, shp), 2799 (w, shp), 2274 (v str, shp), 1953, 1877, 1808 (vw, br), 1496 (w, shp), 1454, 1365 (m, shp), 1344, 1311 (w, shp), 1206 (w, br), 1104 (str, shp), 1026 (m, shp), 910 (w, br), 736, 698 (str, shp), 598 cm^{-1} (m, br).

Monobenzyl Ester of Glutaric Acid (3). The procedure followed that for the synthesis of the monomethyl ester of succinic acid reported by Cason.[44] Glutaric anhydride (10 g, 0.0876 mol) and 9.3 g of benzyl alcohol (0.0856 mol) were heated to 80 °C for 5 h under inert atmosphere with stirring. The half-acid ester formed is purified by base/acid neutralization and distilled under reduced pressure (0.05 mmHg) to yield 7.1 g of **3** (bp 156 °C). ^{1}H NMR (TMS at 0.00 ppm): δ 1.95 (t, 2H), 2.40 (m, 4H), 5.11 (s, 2H), 7.33 (m, 5H), 11.11 (b, 1H). ^{13}C NMR ($CDCl_3$ at 77.00 ppm): δ 31.29, 40.05, 66.54, 73.15, 122.23, 129.15, 138.31. The infrared spectrum was consistent with the structure.

3-(Benzyloxycarbonyl)-*n*-propyl Isocyanate (4). The synthesis of this monomer follows exactly that of compound **2** described above by starting with acid **3**. Bp: 110 °C at 0.05 mmHg. Anal. Calcd: C, 65.8; H, 6.0; N, 6.4. Found: C, 65.9; H, 6.3; N, 6.3. ^{1}H NMR (TMS at 0.00 ppm): δ 1.92 (pentad, 2H), 2.46 (t, 2H), 3.38 (t, 2H), 5.16 (s, 2H), 7.34 (m, 5H). ^{13}C NMR ($CDCl_3$ at 77.00 ppm): δ 26.00, 30.74, 41.92, 66.15, 121.82, 128.01, 128.36, 135.61, 172.10. Infrared (neat): 3679, 3443, (vw, br), 3091, 3067, 3034, 2959, 2889 (w, shp), 2280 (str, shp), 1958, 1877 (vw, br), 1735 (str, shp), 1607, 1587 (vw, shp), 1498 (w, shp), 1456 (m, shp), 1418 (w, shp), 1383, 1357, 1318 (m, shp), 1250 (m, shp), 1162 (str, shp), 1082 (w, shp), 1005 (w, br), 829 (w, shp), 753, 696 (m, shp), 605 (w, shdr), 578 cm^{-1} (w, shp).

4-Isocyanato-2-butanone (5). This monomer was synthesized by starting with levulinic acid purchased from the Aldrich Chemical Co. The general procedure for the synthesis of this monomer is similar to that used for the preparation of compound **2** but with the following modifications. 1,2-Dichloromethane was used for the extraction of the acyl azide. The solvent was removed under an inert atmosphere at 60 °C, and dry toleune was added. The flask was heated to 95 °C for 1 h. Toluene was removed under reduced pressure, and the residue was fractionally distilling using a 5 in. Vigreux column packed with helices (up to 2 in.) at 4 mmHg to obtain **5** bp 58 °C. ^{1}H NMR (TMS at 0.00 ppm): δ 2.20 (s, 3H), 2.74 (t, 2H), 2.55 (t, 2H). ^{13}C NMR ($CDCl_3$ at 77.00 ppm): δ 29.99, 37.36, 43.79, 122.98, 205.35. Infrared (neat): 3684, 3413 (vw, br), 3139, 3045, 3005 (w, shdr), 2958, 2912, (str, shp), 2275, 1715 (str, shp), 1463, 1426, 1401 (m, shp), 1374, 1265, 1169 (str, shp), 988, 944, (m, shp), 878 (str, shp), 822, 778, 751, (m, shp), 619 (shdr, shp), 582 cm^{-1} (m, br).

Synthesis of Functionalized Polyisocyanates. Following the literature,[13] the monomer distilled over CaH_2 was transferred directly into the polymerization flask followed by toluene (5 mL/1 g of monomer). The solution was stirred and cooled to 78 °C, and the initiator solution, NaCN/DMF was added. The solution gelled in less then 10 min, but the polymerization was terminated after 5 h by adding cold methanol (−50 °C). The solid mass was immediately broken up by spatula and washed several times with cold methanol until a white fibrous mass was obtained which was scooped out and vacuum dried at 40 °C. The dry material obtained in this way by using monomers **2** and **4** was dissolved in chloroform, and that from **5**, in CH_2Cl_2. The chloroform solutions were dropped into rapidly stirring methanol at room temperature, and that from CH_2Cl_2 was dropped in cold methanol (−20 °C). After filtering and drying, the white solid was obtained typically in more than 50% yield. Monomer M-1 (**2**) gave poly(3-(benzyloxy)-*n*-propyl isocyanate) (PIET), monomer M-2 (**4**) gave poly(3-(benzyloxycarbonyl)-*n*-propyl isocyanate) (PIES), and monomer M-3 (**5**) gave poly(3-oxobutyl isocyanate) (PIK). Anal. Calcd for PIET: C, 69.02, H, 6.79; N, 7.32. Found: C, 69.05; H, 6.80; N, 7.32. ^{13}C NMR ($CDCl_3$ at 77.00 ppm): δ 28.40, 45.91, 67.72, 72.69, 127.51, 129.29, 138,51, 156.59. Anal. Calcd for PIES: C, 65.68; H, 5.92; N, 6.38. Found: C, 65.88; H, 6.04; N, 6.39. ^{13} NMR ($CDCl_3$ at 77.00 ppm): δ 23.93, 31.06, 66.12, 128.07, 128.43, 136.02, 156.57, 172.16. Anal. Calcd for PIK: C, 53.09; H, 6.24; N, 12.38. Found: C, 52.80; H, 6.44; N, 12.28. ^{13}C NMR ($CDCl_3$ at 77.00 ppm): δ 29.99, 41.48, 43.39, 155.81, 205.98.

The polymerization using $CpTiCl_2OCH_2CF_3$ (which was synthesized following BassoBert[45]) was performed by dissolving the initiator in three drops of toluene followed by the addition of the isocyanate monomer with rapid stirring. The reaction mixture was left standing for 24 h, followed by the addition of methanol to obtain a white solid mass. Attempted polymerization of *n*-hexyl isocyanate, M-1, M-2, and M-3 using this procedure[14] gave polymer only from *n*-hexyl isocyanate and M-1. In M-3 the system turned to a solid mass which was soluble in methanol, while in M-2 the solution darkened but with no viscosity increase. The elemental analyses and NMR and infrared spectra from the polymer obtained from M-1, PIET, was identical to that obtained from the NaCN/DMF method.[13]

Poly(isocyanatobutyric acid) (6). Large pore size palladium/charcoal catalyst was a gift from Johnson-Matthey. Into a 25 mL two neck flask was transferred 48.2 mg of catalyst and 10 mL of dimethylacetamide (DMAc). Then 57.0 mg of PIES was dissolved in 5 mL of DMAc, and this was transferred into an addition funnel attached to the two neck flask. The flask was then attached to a microhydrogenator. Hydrogen was purged to saturate the catalyst. The polymer solution was added to the catalyst flask with stirring. The flask was detached from the microhydrogenator when consumption of hydrogen ceased. The solution was centrifuged, and most of the DMAc was evaporated under high vacuum. The viscous solution, which still appeared to contain some carbon from the catalyst, was transferred onto a Teflon plate, and the remaining DMAc wa evaporated under high vacuum at 40 °C. This left a film of poly(isocyanatobutyric acid), PBIAC, 28 mg. ^{13}C NMR DMSO-d_6 at 39.5 ppm): δ 23.38, 30.97, 155.96, 173.56. FTIR (film): 3600–2250 (br), 2970, 1700 (str), 1610, 1460, 1345, 1170, 1060, 890 (med), 762, 648 cm^{-1} (br). Hydrogenolysis of PIES when performed at 200 psi of hydrogen gave similar results. The absence or low level of the benzyl ester group was confirmed by infrared and NMR spectra by observations at frequencies where this group appeared in PIES (see above).

Poly(styrene-*co*-hydroxystyrene) (7). Styrene was purchased from the Aldrich Chemical Co. Acetoxystyrene was purchased from the Hoechst Celanese Corp. Both the monomers were washed with 10% aqueous NaOH and then with water and then dried and purified by distillation under vacuum. One hundred grams of styrene (0.961 mol), 15.5 g of *p*-acetoxystyrene (0.101 mol), and 0.427 g of azobis(isobutyronitrile) were transferred into a 2 L flask along with 1 L of dry dioxane. The flask was heated at 60 °C for 18 h, after which the reaction mixture was slowly poured into methanol to obtain poly(styrene-*co*-*p*-acetoxystyrene). The copolymer formed is random in nature since the monomer reactivity ratios are $r_1 = 0.80$ and $r_2 = 1.02$.[46] The polymer was analyzed by proton NMR and the integration results at this stage showed it to contain 9 mol % of acetoxystyrene units.

The hydrolysis reaction was carried out by following Ledwidth et al.[11] Typically, 10 g of poly(styrene-*co*-*p*-acetoxystyrene), 1 g of hydrazine hydrate, 2 mL of water, and 400 mL of dioxane were stirred in a 1 L flask for 40 h at 25 °C. The resulting solution was slowly poured into 4 L of methanol. The white polymer obtained was washed with 1 L of methanol and then dried under vacuum in an oven at 70 °C for 3 days. On standing for several months, this copolymer fails to dissolve in solvents which dissolve freshly prepared material, indicating a slow cross-linking reaction.

Decomposition of Poly(isocyanato-*n*-butyric acid) in Buffer Solution. Poly(isocyanato-*n*-butyric acid) (6 mg) was dissolved in 1 mL of pH 7.0 phosphate buffer. The buffer solution contained 10% D_2O. The ^{13}C NMR spectrum recorded after 16 h showed major peaks corresponding to PBAIC at 23.92, 33.06, 47.99, 156.22, and 179.88 ppm and very small peaks at 23.42, 34.05, and 42.36 ppm corresponding to methylene units arsing from the cyclic trimer of PBAIC. NMR spectra recorded after 100 h showed the intensity of the peaks resulting from the trimer to be very intense in comparison to the polymer peaks. Moreover the intensity of the backbone carbonyl peak which appears at 156.22 ppm was reduced considerably.

In a similar experiment performed using a pH 9.5 (borax/sodium hydroxide) buffer, after 14 h of scanning the ^{13}C NMR spectrum showed the intensity of the peaks resulting from the trimer to be considerably higher compared to peaks arising from the polymer.

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