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Synthesis of polymers from 1,3-bishydroxymethyl-2-imidazolidone

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Summary

Copolymers of the title compound with urea, thiourea and toluene diisocyanate were synthesized. The copolymerizations with the urea and thiourea were conducted in water, while the copolymerization with toluene diisocyanate was conducted in dimethylformamide (DMF). All the polymerizations proved to be very exothermic in nature. The resulting polymers proved to be soluable only in dimethylsulfoxide (DMSO), dimethylformamide or concentrated formic acid. Inherent viscosity measurements showed the polymers to be low in molecular weight.

Introduction

While polymers and crosslinking agents based on N-methylol ureas and their derivatives are well known (1-4) and 1,3-bishydroxymethyl-2-imidozolidone (BHI) has been used as a crosslinking agent for cellulostics (5), a sizing agent for fabrics (6) and a crosslinker and stablizer for polyurethanes (7); with the exception of work by Masuoka, et. al. (8,9) concerning the self condensation of BHI catalyzed by metal salts; there is no reported work on the reactivity of BHI in copolymerization reactions. We therefore undertook the synthesis of some copolymers of BHI in order to evaluate such a reactivity, and this paper reports some of our preliminary results.

Experimental

General

All solvents and reagents utilized in this study were reagent grade and were used without further purification. ^{1}H-Nmr spectra were recorded at 90 MHz with a Perkin-Elmer R-32B instrument operating in the CW mode. All spectra were recorded at ambient temperature. IR spectra were recorded with a Digilab FTS 3240E spectrometer operating in the FT mode. Inherent viscosities were determined using a Cannon-Fenske Viscometer. Polymer Tg's were measured with a DuPont 2100 Thermal Analyzer under N_2 at a scan rate of 10^oC/min.

Monomer Synthesis

The BHI was synthesized via a published procedure (10). Formaldehyde (325g of a 37% solution, 4.01 mole) was charged into a 1-liter flask equipped with a thermometer, reflux condenser and mechanical stirrer. The solution was rendered basic (pH = 9) through the addition of aqueous NaOH. Imidazolidone (172.18g, 2.0 mol) was added, with rapid stirring, at such a rate that the reaction temperature did not exceed 60°C. After all the imidazolidone had been added, the reaction was stirred and allowed to come to room temperature over the course of 2-2.5h. The reaction mixture was then stirred and heated at 40°C for 1h to complete the reaction. The water was removed under reduced pressure at 30°C. After 85-90% of the water had been removed the reaction mixture solidified into a white crystalline mass. The crystals were isolated by filtration and thoroughly washed with acetone and cold ethanol. The crystals were dried in vacuo at 35°C for 48h. The yield of white crystals melting sharply at 88.0°C was 96.2%. ^{1}H-Nmr, d_6-DMSO; $\delta = 3.35$ (s.s., 4H); $\delta = 4.53$ (s.s., 4H); $\delta = 5.47$ (b.s., 2H).

Urea Copolymer

BHI (51.1g, 0.35 mol) and urea (21.15g, 0.35 mol) were dissolved in 175 ml of deionized water contained in a 500 ml flask equipped with a mechanical stirrer, reflux condenser and thermometer. Stirring was begun and 3.0 ml of conc. HCl was added all at once. The temperature of the reaction mixture immediately rose to 40°C and a large quantity of white solid precipitated. The reaction mixture was allowed to come to room temperature (~ 1.0h) and was then heated at 65°C for 0.5h to complete the reaction. The solid was isolated by filtration, washed repeatedly with deionized water (6 x 250 ml) followed by ethanol (6 x 200 ml). The polymer proved to be insoluable in all common laboratory solvents including DMSO and DMF. The polymer was soluable in 97% formic acid and in m-cresol. Purification was effected by dissolving the polymer in formic acid and precipitating into a 10-fold excess of deionized water. The solid was collected by filtration and dried in vacuo at 30°C for 72h. The yield of polymer was 97%.

Thiourea Copolymer

Thiourea (26.79g, 0.35 mol) and BHI (51.1g, 0.35 mol) were dissolved in 175 ml of deionized water contained in a 500 ml flask equipped as described above. Concentrated HCl (3.0 ml) was added, however, in this case no immediate exotherm was observed. The solution was heated gently to 50°C, at which point the temperature rose sharply to 70°C and a large quantity of white precipitate formed. The reaction mixture was allowed to stir and come to room temperature over the course of 2.0h. The reaction mixture was then heated at 65°C for 0.5h to complete the reaction. The polymer was removed by filtration and dried in vacuo at 30°C for 72h. As in the urea case the polymer proved insoluable in common laboratory solvents with the exception of DMSO. The polymer was purified by dissolution in 97% formic acid and precipitation into a 10-fold excess of deionized water. The yield of polymer was 96%.

Toluene Diisocyanate Copolymer

BHI (29.01g, 0.2 mol) was dissolved in 160 ml of DMF. Toluene diisocyanate (34.66g, 0.2 mol of an 80/20 2,4/2,6 mixture) was added all at once. The temperature rose very rapidly to 75°C and the viscosity of the solution dramatically increased, at this point the flask was immersed in a cold water bath in order to control the exotherm. The temperature peaked at 78°C and remained there for ~5 min. When the temperature began to decline the cooling bath was removed and the reaction was allowed to proceed for 1h, by which time the reaction temperature had fallen to 25°C. The polymer was isolated by pouring the reaction mixture into 1l of a 50/50 ethanol/water solution. The polymer was isolated by filtration as a large white fibrous mass. Purification was effected by dissolution in DMF and precipitation into ethanol. The polymer was dried in vacuo at 30°C for 72h. The yield was 94%.

Results and Discussion

Figures 1 and 2 show the IR and ^{1}H-nmr spectra of the polymers obtained in this study. The ^{1}H-nmr spectrum of the urea copolymer was not obtained because of this polymers insoluability in common nmr solvents. The absorbances and resonances assigned as shown in the Figures are consistent with the structures assumed for the polymers (11,12).

The inherent viscosities and Tg's obtained for the copolymers are summarized in Table 1.

TABLE 1

Inherent Viscosities and Tg's

Polymer	η_{inh} (dl/g)	Tg (°C)
BHI-Urea	0.10^a	40.3
BHI-Thiourea	0.21^a	40.5
BHI-TDI	0.14^b	-

a. 0.7 g/dl in 95% HCOOH
b. 0.7 g/dl in DMSO

From the results presented in the Table, it is apparent that the polymers are of low molecular weight, but they are also rigid materials as indicated by their moderately high Tg's even at these low molecular weights. An examination of the structure of the polymers shows that they would be expected to have a rigid structure. There are two carbonyl moieties in the polymer backbone that provide geometrical constraints on mobility and amide nitrogens that could provide hydrogen bonding similar to that encountered in nylons (10).

Conclusions

Low molecular weight copolymers of BHI have been synthesized and characterized. All polymerizations were exothermic in nature and produced high yields of polymer. The polymers proved insoluable in common solvents, but were soluable in concentrated formic acid, DMSO or DMF.

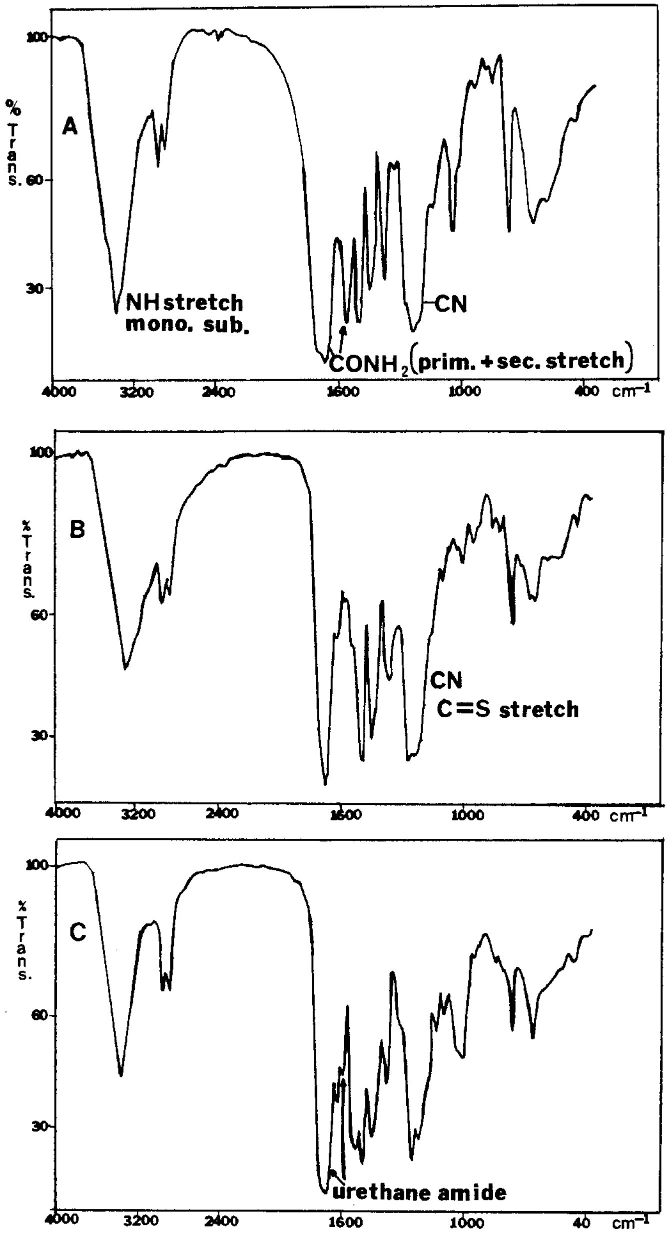

Figure 1: Infared spectra of: A) BHI-Urea copolymer; B) BHI-Thiourea copolymer; C) BHI-TDI copolymer. Spectra were recorded on KBr pellets.

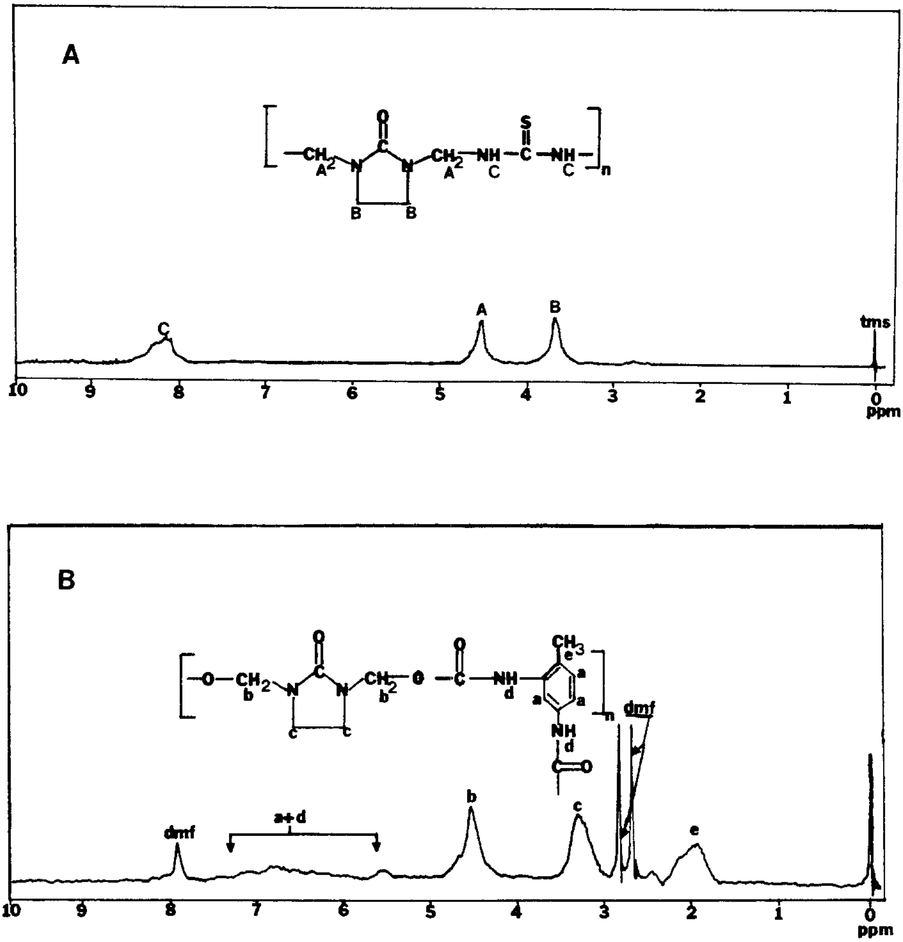

Figure 2: ^{1}H-Nmr spectra of: A) BHI-Thiourea copolymer; B) BHI-TDI copolymer. Spectra were recorded at room temperature in d_6-DMSO.

The spectra obtained show the polymers have the structure expected from a consideration of the chemistry.

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