Polymer Bulletin 31, 637–643 (1993)

Polymer Bulletin

Polymers from 2-oxazolidone and dicarboxylic acids

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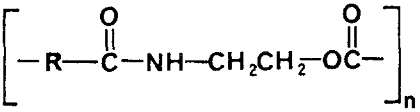
Summary

2-Oxazolidone was reacted at elevated temperature with adipic, isophthalic or sebasic acid. The reaction products were polymeric in nature and range in color from light tan to dark brown. The polymers were not soluble in most common laboratory solvents with the exception of DMF and DMSO. The polymers had moderate inherent viscosities and ^{1}H-NMR and infrared spectra consistent with a polyester-amide chain structure.

Introduction

As part of their studies of the ring-opening polymerizations of iminocarbonates Mukaiyama et al. (1-6) were the first to report that the high temperature reaction between a dicarboxylic acid and 2-oxazolidone or 2-thiazolidone produced polymeric materials. The structure of these polymers was assumed to be that of a polyester-amide as shown in Figure 1.



$$\left[-R-\overset{O}{\overset{\|}{C}}-NH-CH_2CH_2-O\overset{O}{\overset{\|}{C}}- \right]_n$$

Figure 1

However, Mukaiyama et al. gave no data concerning the characterization of these materials. Therefore, in order to more fully understand this reaction and characterize the resulting products, we undertook the investigation that is the subject of this report.

Experimental

All solvents and reagents used in this study were reagent grade and were used without further purification. The ^{1}H-NMR spectra were obtained with a Perkin-Elmer R-32B spectrometer operating at 90 MHz in the CW mode. The infrared spectra were obtained with a Perkin-Elmer 283 IR spectrometer operating in the FT mode. Inherent viscosities were measured with a Cannon-Fenske viscometer at 20°C. Solution concentrations for the inherent viscosity measurements were 0.7 g/dl. Glass transition temperatures were measured with a DuPont 2100 Thermal Analyzer under N_2 at 15°C/min.

Polymer Synthesis

The following example illustrates the method of polymer synthesis employed.

2-Oxazolidone (30g, 0.35 mol) was charged into a 250 ml four-necked round bottom flask equipped with a mechanical stirrer, N_2 inlet, thermometer, Dean-Stark trap and reflux condenser. Isophthalic acid (58.1g, 0.35 mol) was charged into the flask, heating and stirring, under a moderate flow of nitrogen, was begun. The reaction mixture was heated to 210°C over the course of 30 min. A small amount of water (~1ml) was collected in the Dean-Stark trap during this time period. Over the next 30 min. the temperature of the flask contents was raised to 230°C. During this period an additional 4ml of water was collected in the trap. Also, a quantity of a vapor which was noncondensable under the conditions employed [cold (17°C) water cooled reflux condenser] for this reaction, was observed to evolve during this time. Given the proposed polymer structure (Figure 1) is accurate, the vapor is most likely CO_2. The reaction mixture was held at 230°C for 1h. During this time more water was collected, bringing the total volume of water collected to 6.0 ml (theor. = 6.2ml). In addition, more of the noncondensable vapor was observed to evolve during this 1h time period. Heating was stopped and the reaction mixture was allowed to cool. At ~165°C the reaction mixture solidified to a hard, brittle mass. The polymer was broken up and removed from the flask and washed with methanol (3 x 500 ml). The polymer proved to be insoluble in $CHCl_3$, CH_2Cl_2, acetone, THF, toluene, 2-butanone, benzene, diethyl ether and methanol. The polymer was very soluble in N,N-dimethylformamide (DMF). The polymer was purified by reprecipitation from DMF solution into methanol. The purified polymer was dried in vacuo at 30°C for 48h. Yield was determined gravimetrically.

The other polymers were synthesized in the same fashion; with the exceptions that the adipic acid polymer was purified by precipitation into diethyl ether and, because the sebasic acid polymer proved insoluble in DMF, it was purified by precipitation from 60/40 v/v benzene/methanol into excess isopropanol.

Results and Discussion

The polymer yields, inherent viscosities and glass transition temperatures obtained are summarized in Table 1.

TABLE 1

Polymer Yields, Inherent Viscosities and Glass Transition Temperatures

Polymer	Diacid	Yield (wt %)	inh (dl/g)	Tg (^{o}C)
OxIso	Isophthalic	40.2	0.91^{a}	115^{o}
OxAd	Adipic	68.5	0.64^{a}	29^{o}
OxSeb	Sebasic	75.3	1.15^{b}	-20^{o}

a. Measured in DMF b. Measured in 60/40 v/v benzene/methanol

The polymer yields presented in Table 1 are the yields obtained after reprecipitation of the polymers in the nonsolvents previously mentioned. The polymers were characterized as to molecular weight by inherent viscosity measurements. Gel permeation chromatography was not performed because the polymers proved to be insoluble in standard GPC solvents such as THF and $CHCl_3$ and we did not have access to a GPC instrument that used DMF as an eluent. The inherent viscosities obtained show the polymers to be moderately high in molecular weight (7).

The ^{1}H-NMR and IR spectra obtained are shown in Figures 2 and 3. The signals are assigned as shown in the Figures (8,9). The spectra, both ^{1}H-NMR and IR, have the features expected for polymers with polyester-amide structures. For the isophthalic acid comonomer, integration of the signals in the ^{1}H-NMR spectrum (Figure 2A) gives four aromatic protons (δ = 6.80-8.85) and five aliphatic protons (δ = 3.00-5.20). The signal multiplicity shows the triplet expected for the two sets of methylene protons. A triplet is expected because the two sets of methylene protons (H_f and H_e) are not chemically equivalent. However, the difference is not great enough so that two independent triplets can be observed at this spectrometer power. The signal integration is five because the amide proton resonance overlaps the methylene protons resonance. The ^{1}H-NMR spectrum of the adipic acid-oxazolidone polymer (Figure 2B) shows that the two sets of methylene protons from the oxazolidone, H_b and H_c, are observable as independent resonance areas. The signals are broad but give some indication of multiplicity, most likely they are triplets. However, the resolution is insufficient to establish multiplicity with certainty. The H_a proton resonance has a integral intensity of 1 and is a low broad envelope, a characteristic of $N\underline{H}$ or $O\underline{H}$ protons (8). As a result this resonance is assigned to the amide proton as shown. The H_d and H_c resonances are due then to the methylene protons of the adipic acid moiety. The upfield resonance, H_c is a broad, featureless singlet and is due to the interior methylene protons of the adipic acid. The downfield resonance H_d is due to the methylene protons adjacent to the carbonyl functionalties (9,10). Some multiplicity is evident, but the resolution is insufficient to ascertain exactly what the multiplicity may be. In the proton spectrum of the sebasic acid-oxazolidone polymer, Figure 2C, the oxazolidone methylene protons are resolved into two distinct triplets, H_a and H_b. The methylene protons next to the carbonyl functionality in the sebasic acid moiety, H_c, are resolved into a quartet or possibly higher order multiplet. The remaining methylene protons of the sebasic acid moiety occur as two broad envelopes H_d and H_e. The H_d resonance is probably due to the methylene protons on the carbons β to the carbonyl functionalities which could account in some part for the multiplicity in the resonance of the protons on the carbons α to the carbonyl functionalities (H_c).

The infrared spectra of the polymers are shown in Figure 3 A-C. The assignments for the key bands are given in the Figure. The IR spectra clearly have all the features expected for polymers with ester-amide structures. While this fact does not conclusively prove that the polymers are polyester-amides, when coupled with the NMR data it makes a strong argument that the polymers from diacid-oxazolidone reactions do have the proposed structure, that of a polyester-amide.

The glass transition measurements show the expected trend, with the isophthalic acid based polymer having the highest Tg and the sebasic acid based polymer having the lowest Tg. Given that the structure of these polymers is a polyester-amide, which the evidence strongly suggests, an examination of the isophthalic acid polymer chain would produce the expectation of a high Tg or at least the highest Tg of the polymers synthesized in this study. In fact, given the relative rigidity of amide bonds and aromatic rings, it is somewhat surprising that the Tg is not higher. It is possible that the molecular weight of this material is too low for the maximum Tg to be attained, although inherent viscosity suggests otherwise. However, inherent viscosity is not the best measure of a polymer's molecular weight, GPC in an appropriate solvent will be necessary in order to answer this question. The low Tg's of the adipic and sebasic acid based materials reflects the mobility of the alkyl chains in these polymers. Again, whether the Tg's reported represent the true Tg's awaits more accurate determination of molecular weight.

Conclusions

Polymers of moderate molecular weight, by inherent viscosity measure-

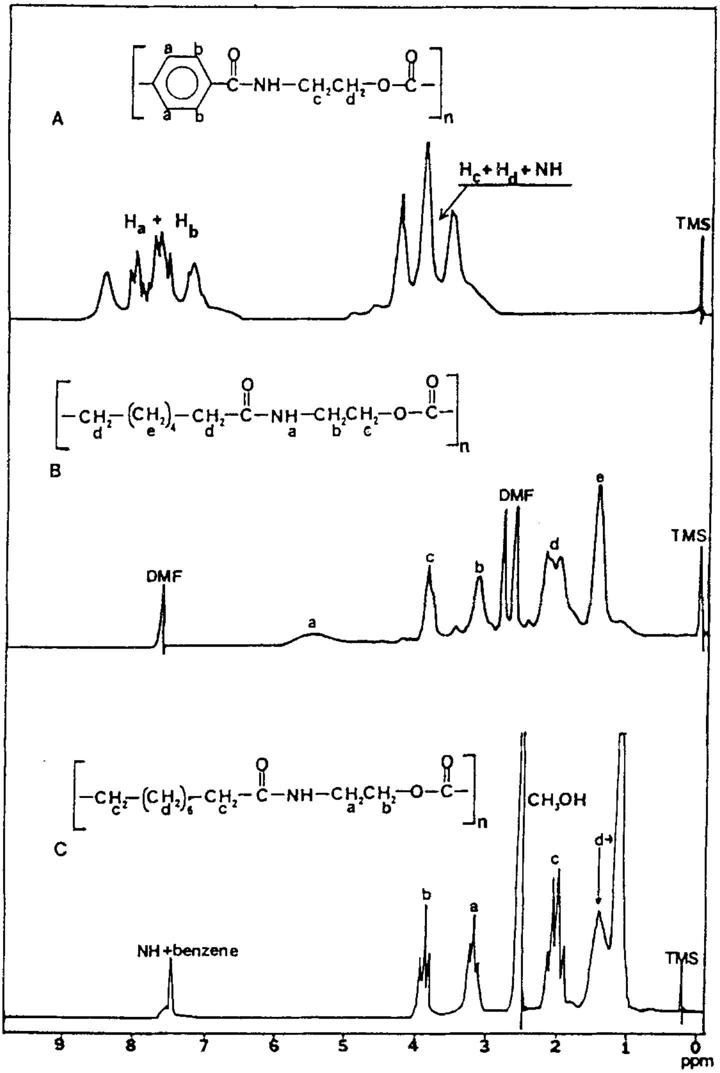


Figure 2: 90 MHz ^{1}H-NMR spectra of: A) Isophthalic acid-oxazolidone copolymer in d_6-DMSO; B) Adipic acid-oxazolidone copolymer in d_6-DMSO; C) Sebasic acid-oxazolidone in d_6-benzene/d_4-methanol.

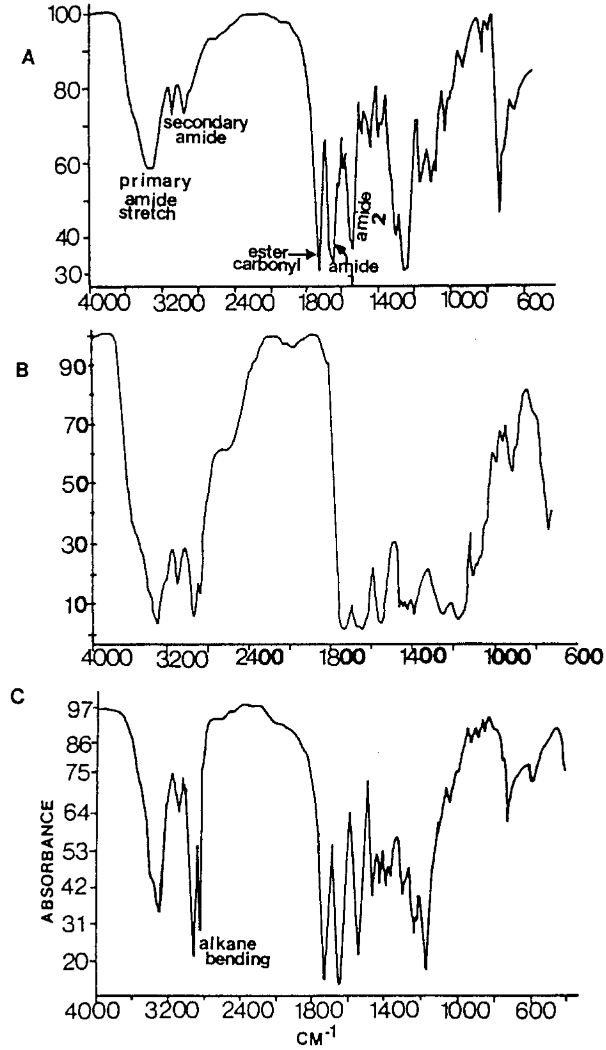


Figure 3: FT-IR spectra of: A) Isophthalic acid-oxazolidone copolymer; B) Adipic acid-oxazolidone copolymer; C) Sebasic acid-oxazolidone copolymer.

ments, can be synthesized from the melt phase reaction of diacarboxylic acids with 2-oxazolidone. The polymers proved to be insoluble in many common laboratory solvents, but soluble in DMF, DMSO or a mixture of benzene and methanol. ^{1}H-NMR and infrared spectroscopy strongly indicate that the polymers have a polyester-amide structure as purposed by Mukaiyama et al. However, more spectroscopic characterization using high field strength NMR instruments and ^{13}C-NMR spectroscopy is underway and will be reported at a later date.

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Accepted November 1, 1993 K