Polymer Bulletin 11, 129–134 (1984)

Polymer Bulletin

Copolymers

Copolymerization of Vinyl Acetate with Methyl N-(1-Cyanopropene-2-Yl)Itaconamate

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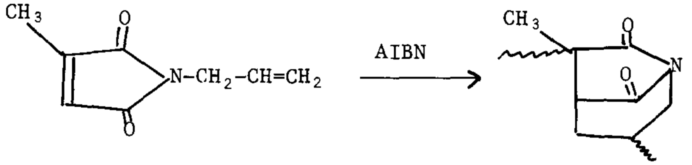
SUMMARY

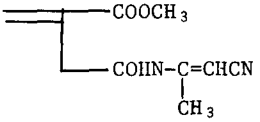
Vinyl acetate copolymerized with methyl N-(1-cyanopropene-2-yl)itaconamate(I) forming low molecular weight copolymer containing about 8% of I. I was prepared by methylating potassium N-(1-cyanopropene-2-yl)itaconamate. The amic acid of the last salt as well as N-(1-cyanopropene-2-yl)maleamic and N-(10cyanopropene-2-yl)citraconamic acids could not be dehydrated to the corresponding imides using acetic anhydride-sodium acetate mixture. High melting, water-soluble polymeric products that could not be crystallized were always the products. These results confirm earlier related studies. Therefore, vinyl containing amic acids having allylic substituents on their nitrogen atoms may not be dehydrated to the corresponding imides by acetic anhydride-sodium acetate mixtures.

INTRODUCTION

In attempts to synthesize monomers containing 1,5-dienes for possible cyclopolymerization (1,2) studies were undertaken to prepare some N-(1-cyanopropene-2-yl)cyclic imides such as N-(1-cyanopropene-2-yl)maleimide, citraconimide, itaconimide, or dimethylmaleimide. These compounds are all 1,5-dienes and were expected to undergo cyclopolymerization reactions similar to related monomers (3,4). Polymers obtained from previously synthesized monomers have been encouraging. For example N-allylmaleimide and N-allylcitraconimide polymerized easily to produce polymers containing high ratios of bicyclic structures in their repeating units.



This paper will discuss the synthesis of four new amic acids and the copolymerization of vinyl acetate with the methyl ester of one of them, namely, methyl N-(1-cyanopropene-2-yl)itaconamate(I)



I

We will also discuss attempts to prepare maleimides, itaconimides, citraconimides, and dimethylmaleimides substituted with allyl containing groups on their nitrogens.

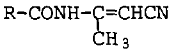
EXPERIMENTAL

Preparation of N-(1-cyanopropene-2-yl)maleamic-, Citraconamic-, Dimethylmaleamic-, and Itaconamic Acids.

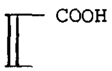
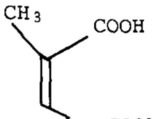
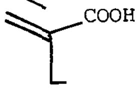
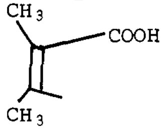
The above amic acids were prepared using a literature method (5). Melting points, percent yields, and elemental analyses of the amic acids are listed in Table I.

TABLE I

Melting Points, Percent Yields, and Elemental Analysis of Some N-(1-cyanopropene-2-yl)amic Acids



$$\text{R-CONH-}\underset{\text{CH}_3}{\text{C}}\text{=CHCN}$$

R	M.P. °C	% Yield		Elemental Analysis C	H	N
	195	90	Calcd.	53.10	4.44	15.50
			Found.	53.30	4.48	15.53
	280	90	Calcd.	55.67	5.15	14.43
			Found.	55.42	5.07	14.21
	198	95	Calcd.	55.67	5.15	14.43
			Found.	55.82	5.17	14.25
	290-291	92	Calcd.	57.60	5.70	13.46
			Found.	57.91	5.68	13.71

Attempted Dehydration of The Prepared Amic Acids of Table I Using Acetic Anhydride and Sodium Acetate. A sample of the amic acid equal to about 0.1 mole was mixed with acetic anhydride (8.0 mole). A catalytic amount of anhydrous sodium acetate (0.006 mole) was added to the reaction mixture which was placed in a 500 ml round bottom flask. The mixture was heated on a water bath for three hours, and was left for the next day. The reaction mixture was poured into 800 ml of cold water with stirring. A black tarry solution was formed when this procedure was applied to N-(1-cyanopropene-2-yl)maleamic-, citraconamic- and itaconamic acids. The black tars were all water soluble. Water was evaporated under reduced pressure. The black tars were freed from acids by stirring them in dilute sodium bicarbonate solution. The products were purified by precipitating them with acetone from aqueous solutions. Repeating this purification procedure resulted in the formation of different melting point solids that had similar infrared spectra. The first crop softened above 300°C while the other materials decomposed at lower temperatures. IR spectra revealed the presence of residual OH groups (3500-2500 cm^{-1}).

Attempted Dehydration of N-(1-cyanopropene-2-yl)dimethylmaleamic Acid.

The titled amic acid was treated with acetic anhydride-sodium acetate according to the previous procedure. Dimethylmaleic anhydride was isolated from the reaction mixture in 55% yield (based on the amic acid). The melting point of the product was 93°C, the same as authentic dimethylmaleic anhydride. The infrared spectrum of the sample was also identical to the spectrum of the authentic compound. Anal. Calc'd. for $C_6H_6O_3$: C,57.10; H,4.70; N,0.00; Found: C,57.23; H,4.80; N,0.0.

Preparation of Methyl N-(1-cyanopropene-2-yl)itaconamate.

10 g (0.04 mole) of dry potassium N-(1-cyanopropene-2-yl)itaconamate (prepared from the corresponding amic acid and potassium hydroxide), excess iodomethane (0.2 mole), 1 g (0.003 mole) of 18 crown-6, and 150 ml of dry acetone were placed in a 500 ml round-bottom flask. The mixture was refluxed for 38 hours. The reaction mixture was filtered and the filtrate was evaporated. The precipitate was washed with water, and recrystallized from ethanol to obtain 5.75 g (64.2%) of a white solid that melted at 141°C. The infrared spectrum of this material had no OH absorption, but revealed the following peaks: 3200 cm^{-1} (amide NH), 2200 cm^{-1} (CN), 1620 cm^{-1} (amide C=O), 1725 cm^{-1} (ester C=O), and 1650 cm^{-1} (olefin stretch). ^{1}H-NMR (DMSO-d_6):δ2.50 (s,3H,CH_3-C=C), δ3.51 (s,3H,CH_3-O), δ6.02 (d,2H,CH_2=C), δ11.50 (s,H, C=CHCN). Anal. Calc'd. for $C_{10}H_{12}N_2O_3$: C,57.69; H,5.76; N,13.46; Found: C,57.64, H,5.81; N,13.48.

Copolymerization of Methyl N-(1-cyanopropene-2-yl)itaconamate With Vinyl Acetate.

A polymerization bottle was charged with: 0.8 g (0.038 mole) of I, 60 ml of freshly distilled THF, 3.26 g (0.038 mole) of vinyl acetate, and 40 mg. of AIBN. The bottle was purged with argon before stoppering. The container was immersed in a bath at 70°C for 3 hours. Then the solvent was evaporated under reduced pressure leaving a viscous transparent polymeric residue. The residue was purified by dissolving it in a small amount of acetone and then reprecipitating it by adding water. The softening point of the product was 120-150°C. IR(KBr): 3200 cm^{-1}(NH), 2200 cm^{-1} (CN), 1720 cm^{-1}(ester C=O), 1650 cm^{-1}(amide C=O). Anal. Calc'd. for 1: 12 mole ratio of the itaconamate ester to vinyl acetate: C,56.98; H,6.82; N,2.33; Found: C,56.56, H,7.02, N,2.26. Intrinsic viscosity in chloroform was 0.17.

RESULTS AND DISCUSSION

Previous work with substituted maleimides revealed that N-allylmaleimide(3,6) could not be prepared by the conventional method of dehydration of N-allylmaleamic acid using acetic anhydride-sodium acetate, phosphorous trichloride, or thionyl chloride. A polymeric product was formed, which had been separated to different molecular weight fractions having different softening points; but they all showed identical elemental analyses and IR spectra. Attempts to prepare N-allylcitraconimide(4) by the dehydration of N-allyl citraconamic acid were not successful. A recent paper (7) reported the preparation and polymerization of several N-substituted itaconimides, but attempts to prepare N-allylitaconimide by the dehydration of the corresponding amic acid failed, and polymer resins formed instead. In the present studies N-(1-cyanopropene-2-yl)maleamic-, citraconamic-, itaconamic-, and dimethylmaleamic acids were prepared and allowed to react with a hot acetic anhydride-sodium acetate mixture. None of these acids produced the corresponding imide. N-(1-cyanopropene-2-yl)imides derived from the above mentioned amic acids were of interest with respect to potential cyclopolymerizabilities. It is interesting to note that N-(1-cyanopropene-2-yl)-

dimethylmaleamic acid produces dimethylmaleamic anhydride when treated with acetic anhydride-sodium acetate mixture, while the other amic acids gave water soluble polymeric residues of different molecular weights. IR spectra of the residues showed broad peaks with some OH and NH absorptions. The vinylic absorptions at 1650 cm^{-1} however, were not present indicating their saturation during polymerization. The difficulty in producing imides from such amic acids may be due to the high polymerization reactivity of the corresponding imides at the reaction conditions employed. The expected N-(1-cyanopropene-2-yl)imides might have formed, but polymerized instantaneously to form bicyclic units among other forms of polymers. It seems that some copolymerization between the amic acids and their corresponding imides has also occurred since the residues revealed some OH and NH absorptions in their IR spectra. In the case of dehydration of N-allylmaleamic acid(6) using a acetic anhydride-sodium acetate mixture, the resulting polymeric residue showed elemental analysis, NMR, and IR spectra very similar to those of poly(N-allylmaleimide) prepared from pure monomer made by another method. These experiments show that it is not possible to prepare maleimides, citraconimides, itaconimides, and dimethylmaleimides having allylic groups on their nitrogens by this method. Fusion of N-(1-cyanopropene-2-yl)maleamic-, citraconamic-, itaconamic and dimethylmaleamic acids yielded dark infusible solids which could not be distilled or recrystallized so as to obtain the corresponding imides. Similar imides have been prepared by the fusion of the amic acid followed by distillation of the melt under reduced pressure(3). It is our conclusion that whenever the substituents on the nitrogen of maleamic, citraconamic, and itaconamic acids contain an allylic group, their cyclization to the corresponding imides may not be successful using an acetic anhydride-sodium acetate mixture. Monomer I was prepared by refluxing potassium N-(1-cyanopropene-2-yl)itaconamate with excess iodomethane in acetone. The pure methyl ester I copolymerized with vinyl acetate yielding a copolymer that had I incorporated in the ratio of 1/12. It is interesting to mention that I could be contaminated with its isomer II. However, based on the sharp melting points of I and of its precursor (the amic acid), in addition to other results (8) , we believe that isomer I is predominant. The composition of the copolymer was calculated by comparing the areas of CN absorptions in the IR spectra of both the monomer and the copolymer. The area of the peak corresponding to the nitrile absorption was found to decrease to 1/12 of its original area (see Figures 1 and 2). Furthermore, elemental analysis of the copolymer indicated the same ratio. The intrinsic viscosity of the copolymer in chloroform was 0.17, indicating a low molecular weight. In fact attempts to prepare thin films of the polymer resulted in brittle materials that easily cracked. Vinyl acetate is known to copolymerize with several vinylic monomers free radically to yield materials of versatile uses. Its copolymerization with I however, seemed not to be favorable. It is interesting to note that I did not homopolymerize free radically or anionically using AIBN or butyllithium as initiators. In this regard the itaconamate methyl ester resembles N-substituted maleamic acids and their corresponding esters which are known to resist homopolymerization by free radical methods(9).

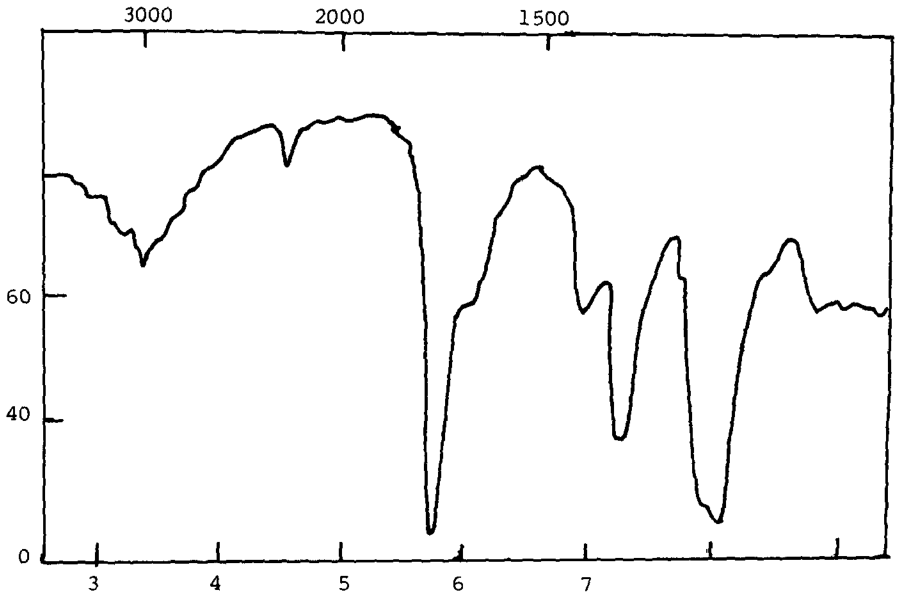
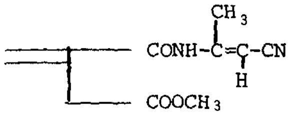


Figure 1: IR spectrum of poly[vinyl acetate-co-methyl N-(1-cyanopropene-2-yl)itaconamate]



$$\mathrm{CONH{-}\overset{CH_3}{C}{=}\underset{H}{C}{-}CN}$$
$$\mathrm{COOCH_3}$$

II

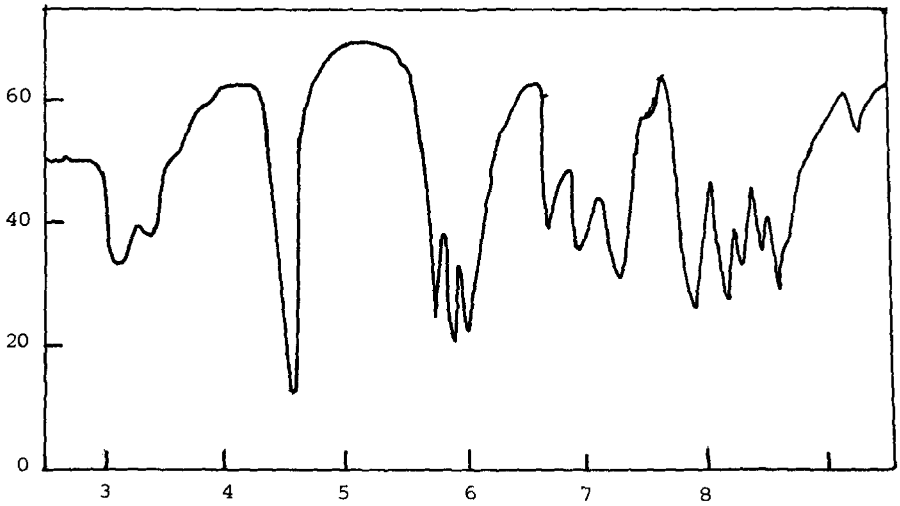


Figure 2: IR spectrum(KBr) of methyl N-(1-cyanopropene-2-yl)-itaconamate.

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Accepted November 3o, 1983