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Akio Takahashi[a]; Sung Ki Lee[a]
[a] Hooker Chemicals and Plastics Corporation, Niagara Falls, New York

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Alternating Copolymers from Alkyleneimines. II. Copolymers from Ethyleneimine and α,β-Unsaturated Acids

AKIO TAKAHASHI and SUNG KI LEE

Hooker Chemicals and Plastics Corporation
Niagara Falls, New York 14302

ABSTRACT

New alternating copolymers are obtained between ethyleneimine which is nucleophilic and α,β-unsaturated acids that are electrophilic. The alternating structure was identified by IR, NMR, and elemental analyses. A reaction mechanism is elucidated in the light of polymer structure which involves a ring-opening reaction of ethyleneimine and a hydrogen transfer to the double bond of α,β-unsaturated acid which is similar to the Michael-type addition reaction. A terpolymer from ethyleneimine, methacrylic acid, and phthalic anhydride was also obtained. It indicates that the two pairs of acid/base copolymer species are cross-propagated and also that the mechanisms involved in both the polymerization of ethyleneimine with dicarboxylic anhydride and of ethyleneimine with α,β-unsaturated acid are basically similar to each other.

INTRODUCTION

The polymerization of alkyleneimines involves a ring-opening reaction catalyzed exclusively by acids [1], while α,β-unsaturated acids undergo polymerization through the π-electron activation, generally by free-radical initiators. Therefore, it has been difficult to obtain a copolymer from these two monomers.

This paper describes alternating copolymers of ethyleneimine and α,β-unsaturated acids such as acrylic and methacrylic acid [2]. The polymerization requires no catalyst and follows a similar reaction mechanism to that previously proposed for the formation of ethyleneimine–dicarboxylic anhydride alternating copolymers [3]. However, the present mechanism seems to involve an extra reaction step, i.e., a hydrogen-transfer reaction to the acrylic double bond.

Such a Michael-type hydrogen-transfer reaction has been proposed by Breslow et al. for the polymerization of acrylamide to poly-β-alanine [4] and recently by Saegusa et al. for poly-β-propiolactone from acrylic acid [5].

EXPERIMENTAL

Monomers and Solvents

Ethyleneimine, acrylic acid, and methacrylic acid were obtained commercially and purified by fractionation. Commercially obtained solvents were distilled, and the fractions distilling at their literature boiling points were collected for use.

Polymerizations

The solution of ethyleneimine in a dropping funnel was added to the equimolar solution of acrylic or methacrylic acid. The reaction was carried out in a nitrogen atmosphere at 20-25° C with stirring. When the addition was over, stirring was continued further for several hours at 25-30° C.

The reaction solution was poured into diethyl ether, filtered, washed with fresh ether, and dried at 70° C in vacuo to constant weight.

Characterizations

Polymers were analyzed for carbon, hydrogen, and nitrogen. The intrinsic viscosity was measured at 25° C in either water or trifluoroacetic acid as a solvent. The structures of the polymers were determined by IR spectra (KBr pellet) and NMR (60 MHz) spectra from solutions in D_2O, CF_3COOH, or DMSO.

RESULTS AND DISCUSSION

Structure of Polymers

Since ethyleneimine and α,β-unsaturated acid undergo a violent reaction in bulk, a number of solvents were used as reaction medium. In a solvent of a high dielectric constant such as alcohols, the reaction proceeds rapidly to give a colorless resin which is soluble in water, methanol, and formic acid but insoluble in acetone, diethyl ether, and carbon tetrachloride. On the other hand, the reaction proceeds somewhat more slowly in a solvent of low dielectric constant such as p-dioxane, yielding a white solid polymer which is soluble in water but insoluble in most of common organic solvents. The results are summarized in Table 1.

Instead of acrylic acid, methacrylic acid was copolymerized with ethyleneimine. The reaction proceeded similarly to that with acrylic acid. A terpolymerization was also carried out, part of the methacrylic acid being replaced with phthalic anhydride which was previously shown [3] to copolymerize with ethyleneimine. These polymers

TABLE 1. Copolymerization of Ethyleneimine and Acrylic Acid in Various Solvents[a]

Solvent	Dielectric constant ϵ^b	Yield (%)	State
Dimethylformamide	37.6	90	Colorless resin
Ethanol	24.3	90	Colorless resin
Ethylacetate	6.02	95	Semisolid
Diethyl ether	4.34	96	White solid
p-Dioxane	2.209	98	White solid

[a] Equimolar amounts of ethyleneimine and acrylic acid, and three times of solvent by weight were used.

[b] Dielectric constant of solvent at 25°C [6].

TABLE 2. Copolymers from Methacrylic Acid and Phthalic Anhydride[a]

Monomers			Elemental analyses						
			Found			Calcd[c]			
Type[b]	Amt (mole)	Yield (%)	C (%)	H (%)	N (%)	C (%)	H (%)	N (%)	Inherent viscosity (η)
EI-AA	0.3-0.3	98	48.24	8.52	11.00	52.17	7.83	12.17	0.13
EI-MA	0.3-0.3	95	54.42	8.55	10.83	55.81	8.52	10.85	0.10
EI-MA-PA	0.3-0.15-0.15	85	60.06	6.15	10.29	–	–	–	0.25[d]
EI-Manh	0.3-0.3	93	48.79	6.05	10.57	51.06	4.96	9.93	Insoluble

[a] Reactions were carried out in three times of p-dioxane by weight based on monomers at 20-30°C for 3-4 hours.

[b] Monomers: EI, ethyleneimine; AA, acrylic acid; MA, methacrylic acid; phthalic anhydride; Manh, maleic anhydride.

[c] Based on the monomers used, i.e., equimolar composition.

[d] In trifluoroacetic acid at 25°C.

were analyzed and compared with the copolymer of ethyleneimine and acrylic acid in Table 2. The copolymer of ethyleneimine and acrylic acid is a white solid and quite hydroscopic, although it remains a powder after absorbing water. The water absorbed in the polymer is very difficult to remove. The polymer should be dried at about 100°C in vacuo for a long period before analysis. Although analysis of the copolymer always gives low values for carbon and nitrogen, due to the hygroscopic nature of the polymer, these values were close to the equimolar composition of the two monomers. On the other hand, the copolymer from methacrylic acid is less hygroscopic, and thus elemental analysis was in good agreement with the values calculated for the equimolar composition.

An ethyleneimine–methacrylic acid–phthalic anhydride terpolymer was also obtained, and it was confirmed that it is not a mixture of copolymers. The ethyleneimine–methacrylic acid copolymer is soluble only in water, whereas the ethyleneimine–phthalic anhydride copolymer is insoluble in water but soluble in trifluoroacetic acid. The terpolymer obtained is readily soluble in trifluoroacetic acid and also in water but with some difficulty, leaving a small amount of insoluble material. The water-insoluble fraction was identified as the ethyleneimine–phthalic anhydride copolymer by IR and NMR.

The IR spectrum of ethyleneimine–acrylic acid copolymer indicated the presence of ester-type carbonyl group at 1720 cm^{-1}. However, the presence of an amide-type carbonyl group was not conclusive but was observed in the IR of ethyleneimine-phthalic anhydride copolymer [2]. On the other hand, the existence of both amide and ester carbonyl groups was observed in the IR spectrum of ethyleneimine–methacrylic acid–phthalic anhydride terpolymer.

The equimolar composition of copolymers, or the alternating nature of the composition, was also confirmed by NMR analysis as shown in Figs. 1-3. The NMR spectrum of ethyleneimine–acrylic acid copolymer (Fig. 1) shows only one major peak centered at δ 4.0-2.0, along with very small peaks at δ 6.3, δ 5.7, δ 5.6 and δ 4.1 ppm. The broad and major peaks at δ 4.0-2.0 are assigned to the protons of $-CH_2O-$, $-CH_2NH-$, and $-CH_2CO_2-$, respectively. The small signals at δ 6.3 and δ 5.6 ppm are assigned to the vinyl protons of alkyl acrylate at the polymer chain end, since these peaks were noticeable at higher spectrum amplitude and appeared stronger in a lower molecular weight polymer. The peaks at δ 5.7 and δ 4.1 are probably spinning bands.

The NMR spectrum of the ethyleneimine–methacrylic acid copolymer, shown in Fig. 2, shows peaks at δ 5.7 and δ 5.48 due to the vinyl

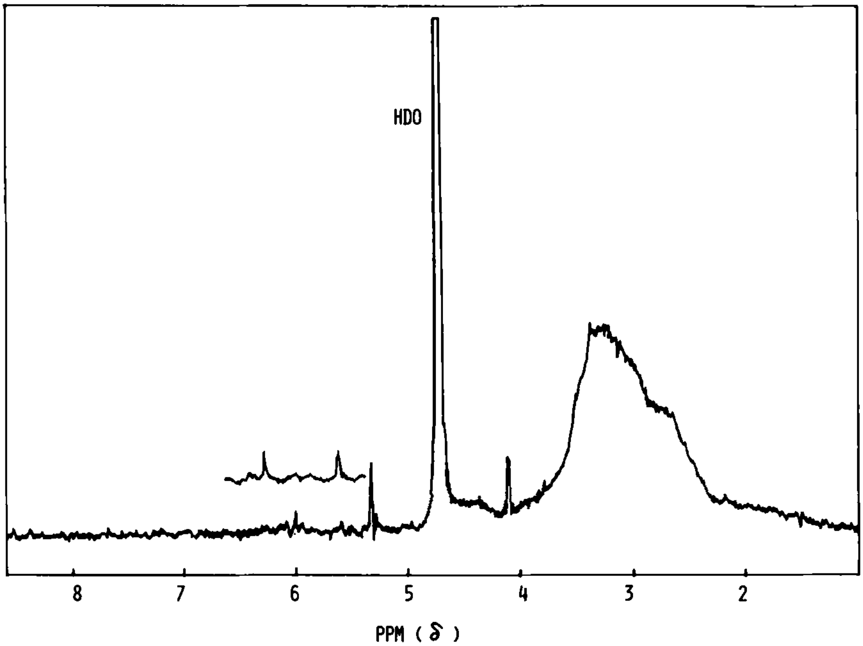


FIG. 1. NMR spectrum of ethyleneimine–acrylic acid copolymer in D_2O (60 MHz).

protons of methacrylate at the polymer chain end, at δ 3.8-2.6 due to the protons of $-OCH_2-$, $-CH_2NH-$ and $-CH_2CO_2-$, and at δ 1.9 due to the methyl protons of methacrylic acid.

The NMR spectrum of ethyleneimine–methacrylic acid–phthalic anhydride terpolymer (Fig. 3) shows strong signals centered at δ 8.0 due to the aromatic protons, weak peaks at δ 6.48 and δ 5.95 assigned to the vinyl protons of methacrylate at the polymer chain end, broad and strong peaks at δ 5.2-3.5 due to the protons of $-OCH_2-$, $-CH_2NH-$ and $-CH_2CO_2-$, and at δ 2.1 due to the methyl protons of methacrylic acid.

It was also found that the integrated ratios among the different protons are in good agreement with the values estimated based on the molar ratio of monomers used.

Although IR and NMR analyses of some polymers indicated the presence of small amounts of N-2-carboxyethyl group ($>NCH_2CH_2COOH$) or betaine ($>\overset{+}{N}HCH_2CH_2COO^-$), overall analytical results best rationalize the structure EI-US for the copolymer of ethyleneimine and α,β-unsaturated acid as a major reaction product.

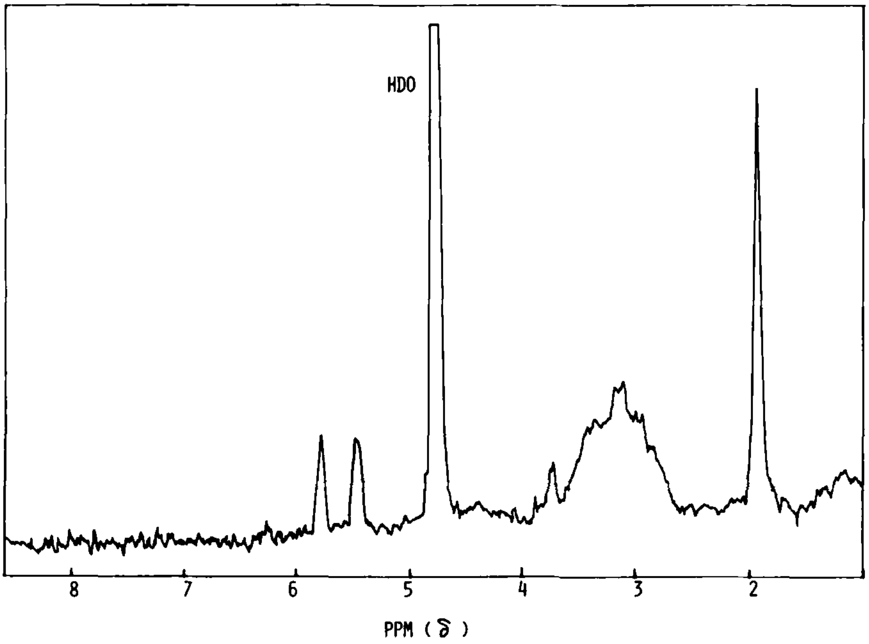


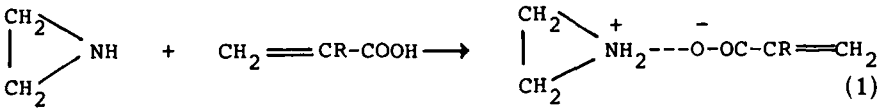
FIG. 2. NMR spectrum of ethyleneimine–methacrylic acid copolymer in D_2O (60 MHz).

$$CH_2{=}CR{-}COO\sim\sim\sim({-}CH_2{-}CH_2{-}NH{-}CH_2{-}CHR{-}COO{-})_n\sim\sim\sim CH_2{-}CH_2{-}NH_2$$

EI-US

Reaction Mechanism

Since ethyleneimine is a base, whereas α,β-unsaturated acid is an acid, salt formation would be the first step in the reaction between these monomers. In fact, the dissociation constants of both ethyleneimine and acrylic acid [7] suggest that 99% of these monomers are present as a salt form (I).



(1)

I

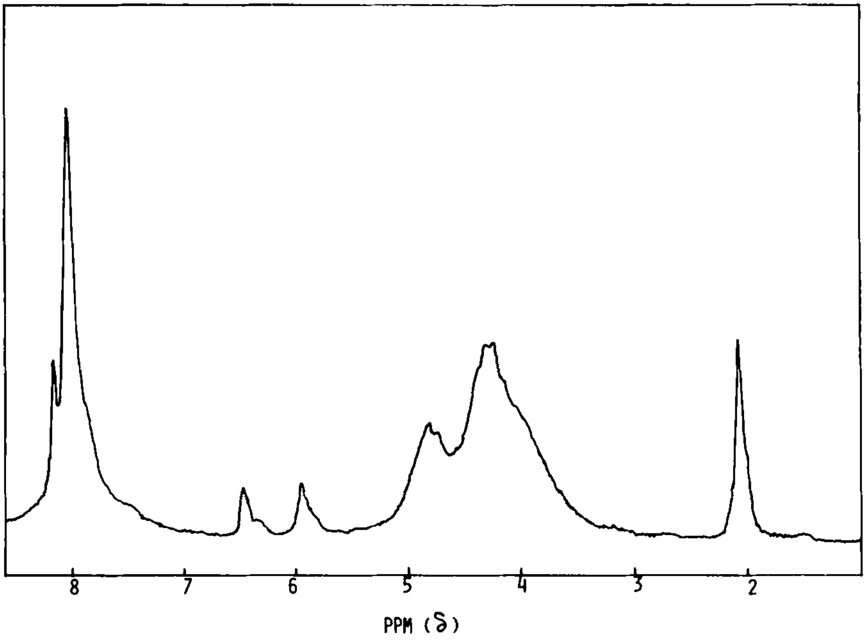
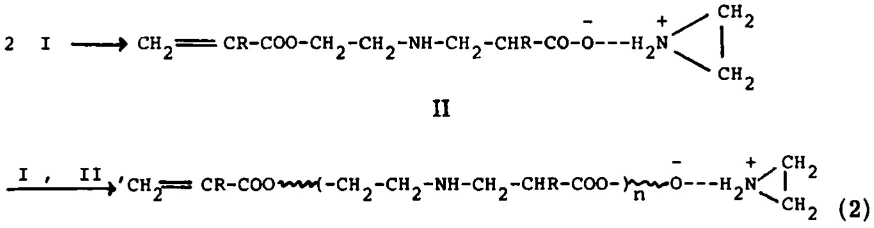


FIG. 3. NMR spectrum of ethyleneimine–phthalic anhydride–methacrylic acid terpolymer in CF_3COOH.

The next step would involve a Michael-type addition reaction between two molecules of salt I. The hydrogen transfer takes place from the nucleophilic ethyleneimine to the double bond of the electrophilic α,β-unsaturated acid, resulting in simultaneous ring opening of ethyleneimine. Thus, the chain propagation involves the Michael-type addition reaction in a successive manner.

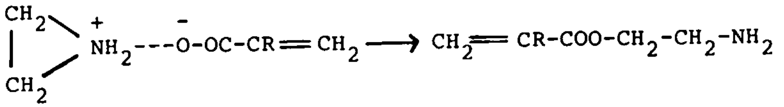


II

III

(2)

An alternative mechanism would involve a formation of aminoalkyl acrylate (IV) from I through the ring opening of base-acid salt. This would be an alternative initiation mechanism.



(3)

I IV

Then, the propagation mechanism would be the Michael-type addition reaction between aminoalkyl acrylates IV as shown in Eqs. (4) and (5).

$$2\ \mathrm{IV} \longrightarrow \underset{\mathrm{V}}{CH_2{=}CR{-}COO{-}CH_2CH_2{-}NH{-}CH_2{-}CHR{-}COO{-}CH_2CH_2{-}NH_2} \qquad (4)$$

$$\mathrm{V} \rightleftharpoons CH_2{=}CR{-}COO$$

$$\underset{\mathrm{VI}}{\sim\sim(-CH_2{-}CH_2{-}NH{-}CH_2{-}CHR{-}COO-)_n\sim\sim CH_2{-}CH_2{-}NH_2} \qquad (5)$$

These mechanisms are basically similar to each other. The difference would be whether the hydrogen transfer takes place simultaneously with or after the ring opening of ethyleneimine. Since the polymerization is exothermic, requiring external cooling to maintain the reaction at room temperature, and seems to proceed quite rapidly, the reaction species involved in the polymerization should be chemically quite a reactive one. On the other hand, it is assumed that I is chemically more reactive than IV, since the former is known to be a reactive intermediate in the ring-opening reaction of ethyleneimine catalyzed by acids leading to a free amine compound such as IV.

Therefore, it can be concluded that the copolymerization by the mechanism of Eq. (2) should be the dominant one, whereas that by (4) would be complementary, since the ring-opening of ethyleneimine would take place throughout the reaction period.

However, the latter mechanism probably becomes an important factor at a later stage of polymerization. In fact, the formation of free amine should be a cause of rate reduction of polymerization.

Such a free amine also should form an inactive salt whenever a free acid is available, thus terminating the polymer chain from further growth.

The results of terpolymerization of ethyleneimine, methacrylic acid, and phthalic anhydride indicate that both mechanisms involved in the copolymerization of ethyleneimine and dicarboxylic anhydride, and ethyleneimine and α,β-unsaturated acid can be operative side by side and thus allow both species to cross-propagate each other. These view points are further supported by the results of copolymerization between ethyleneimine and maleic anhydride, which is an unsaturated dicarboxylic anhydride. As expected, the copolymer obtained from ethyleneimine and maleic anhydride was insoluble and infusible, indicating that it is highly crosslinked.

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