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# Preparation and Characterization of Water-Soluble Copolymers of *N*-Maleyl Glycine with Acrylic Monomers

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# PREPARATION AND CHARACTERIZATION OF WATER-SOLUBLE COPOLYMERS OF *N*-MALEYL GLYCINE WITH ACRYLIC MONOMERS

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## ABSTRACT

Two types of copolymers based on *N*-maleyl glycine with acrylic acid and acrylamide were synthesized. Radical copolymerizations were performed in dioxane at 70°C with AIBN as the initiator. The monomer reactivity ratios were determined using the Kelen–Tüdös method. FT-IR,

$^1$H-NMR, and $^{13}$C-NMR spectroscopy as well as elemental analysis were used for the characterization of the copolymers. The comonomer content of the copolymers and the reactivity ratios were calculated from these data.

## INTRODUCTION

Water-soluble polymers are of great importance and of great interest from the scientific and practical point of view. They are used in technology as flocculating agents for wastewater purification, concentration and extraction of metals, reduction of hydrodynamic resistance, as structure formers of soils, and so on. In medicine and biology they are widely applied as plasma substitutes, for stabilization and purification of some ferments, and for the controlled release of drugs [1–6].

Attention is paid mainly to the hydrodynamic properties of the polyacids, polybases, nonionic hydrophilic high-molecular-weight compounds, among which the intrinsic viscosity of considered in greater detail [7].

Poly(acrylic acid) (PAA) and its copolymers were widely used [8, 9]. PAA is a weak polymeric acid and according to its chemical properties it behaves like a multibasic saturated acid. The dissociation constant $pK_a$ depends on the nature of the solvent, the neutralization agent, the concentration of the solution, the chain microstructure, and to a small extent on the relative molecular mass [10].

Poly(acrylamide) (PAAm) is also widely used in many fields. It is worth noting that the polymer, unlike the monomer, is not toxic [11]. As a consequence of the nonionic character of poly(acrylamide), its viscosity remains constant during a change of pH from 0 to 10. At pH $>$ 10 the polymer undergoes hydrolysis and the specific viscosity increases sharply.

The peculiarity of PAAm in comparison with other amidic polymers of the vinyl series is the fact that its amide group is not substituted and the polymer is subject to hydrolysis and that the polymer chains do not contain hydrophobic side groups. The presence of amide and carboxyl groups in the chains of the dry polymer must lead to an intense intermolecular interaction at the expense of hydrogen bonds between the chains [12].

In this paper we report the synthesis of poly(acrylic acid-*co*-*N*-maleyl glycine) and poly(acrylamide-*co*-*N*-maleyl glycine) by radical polymerization as well as their characterization and the determination of monomer reactivity ratios.

## EXPERIMENTAL

### Reagents

The comonomer *N*-maleyl glycine (MG) was prepared according to a published method [6]. Acrylic acid (Merck) and acrylamide (Merck) were purified by distillation and crystallization, respectively. AIBN was purified by recrystallization from methanol [13]. All the other reagents were used as received.

## Copolymerization

The copolymerization of MG with acrylic acid (AA) and acrylamide (AAm) was carried out in dioxane at 70°C and AIBN as the initiator for 12 hours.

The general procedure was as follows: Acrylic acid (1.3 mmol) dissolved in 1 mL of dioxane was added to 1.3 mmol of maleyl glycine and 0.5 mol% of AIBN at 70°C for 12 hours. The ampule was degassed three times with freeze cycles under nitrogen. The copolymers obtained were filtered off and washed with ether. They were collected and dried in vacuo up to constant weight.

## Measurements

The melting points were determined with a Büchi Unimelt apparatus. The elemental analyses were carried out with a Carlo Erba 1106 analyzer. FT-IR and $^1$H-NMR spectra were recorded on a Perkin-Elmer Model 1818 and Bruker AC 250 spectrometer, respectively.

Viscosity measurements were made using an Ostwald microviscometer (manual for relative measurements) with aqueous solutions of copolymers (0.025-0.040 $g \cdot mL^{-1}$) at pH 5, unbuffered (30°C, 0.1 M NaCl).

# RESULTS AND DISCUSSION

## Synthesis and Characterization of Copolymers

Two copolymer systems were investigated and the reactivity ratios were determined (see Fig. 1).

The radical copolymerizations of *N*-maleyl glycine (MG) with acrylic acid (AA) were conducted in dioxane under several feed monomer compositions. The results are summarized in Table 1. The weight ratios of acrylic acid to maleyl glycine in the copolymers were calculated from the C/N weight percent ratio determined by elemental analysis (see Table 1). These calculations showed that the copolymer contained 0.5 mol fraction maleyl glycine when using an initial monomer feed ratio of 1:1 (see Copolymer 1, Table 1).

The yields of copolymers decreased as the feed monomer ratio increased (except for Copolymer 9, Table 1).

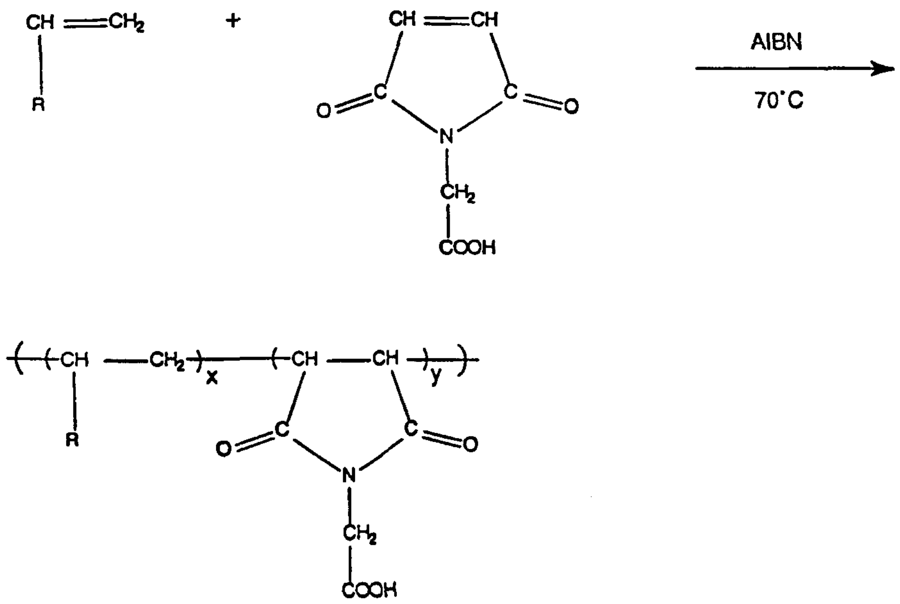
The resulting copolymers were soluble in solvents such as methanol, pyridine, water, and DMSO.

The $^1$H-NMR, $^{13}$C-NMR, and FT-IR spectra of the copolymers obtained in different solvents show that no olefinic groups remained. This suggests that monomers were not occluded in the copolymers (see Figs. 2 and 3).

The FT-IR spectra of the copolymers P(AA-*co*-MG) prepared in dioxane show stretching bands at 3500 $cm^{-1}$ ($-OH$ of $-COOH$ group), 2955 $cm^{-1}$ ($C-H$ of $-CH_2$), 1770 $cm^{-1}$ ($-C=O$ of imide), 1700 $cm^{-1}$ ($-C=O$ of $-COOH$), and 1422 $cm^{-1}$ ($-C-N$ of imide rings).

$^1$H-NMR spectra (250 MHz, $D_2O$, in ppm) show resonances at $\delta$ = 1.5-2.2 ($CH_2$ of AA); at $\delta$ = 2.35-2.6 ($-CH$ of AA), at $\delta$ = 3.0-3.5 ($-OH$); at $\delta$ = 3.5-4.2 ($-HC-CH-$); at $\delta$ = 4.2-4.4 ($-CH_2COOH$); 5.0 ($H_2O$) (see Fig. 2).

$^{13}$C-NMR spectra (62.9 MHz, $CD_3OD$, in ppm) show resonances at $\delta$ = 35 ($-CH_2CH$); $\delta$ = 42 ($-CH_2COOH$); $\delta$ = 43-50 ($-CH-CH-$ and $-CH-$ of



R = COOH(AA)

R = CONH$_2$ (AAm)

FIG. 1. Homo- and copolymerization of *N*-maleyl glycine with acrylic acid and acrylamide by radical polymerization.

TABLE 1. Experimental Data of the Radical Copolymerization of *N*-Maleyl Glycine (MG) with Acrylic Acid (AA) at 70°C and 12 Hours in Dioxane

| Copolymer | *f* | MG, mmol | AA, mmol | AIBN, mg | Solvent, mL | Yield, % | mp, °C | Copolymer composition,[a] MG:AA |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.50 | 1.3 | 1.3 | 2.13 | 1.0 | 85.2 | 330 | 0.50:0.50 |
| 2 | 0.33 | 0.7 | 1.3 | 0.16 | 0.7 | 80.3 | 310 | 0.38:0.62 |
| 3 | 0.66 | 1.3 | 0.7 | 0.16 | 0.7 | 74.4 | 320 | 0.60:0.40 |
| 4 | 0.75 | 1.0 | 0.3 | 0.10 | 0.5 | 82.5 | 330 | 0.68:0.32 |
| 5 | 0.25 | 0.3 | 1.0 | 0.10 | 0.5 | 90.2 | 320 | 0.32:0.68 |
| 6 | 0.90 | 0.9 | 0.1 | 0.82 | 0.4 | 62.5 | 300 | 0.84:0.16 |
| 7 | 0.80 | 1.1 | 0.3 | 0.11 | 0.5 | 72.5 | 300 | 0.71:0.29 |
| 8 | 0.10 | 0.1 | 0.9 | 0.82 | 0.4 | 70.7 | 340 | 0.15:0.85 |
| 9 | 0.20 | 0.3 | 1.1 | 0.11 | 0.5 | 90.7 | 340 | 0.17:0.83 |

[a] Determined from elemental analyses.

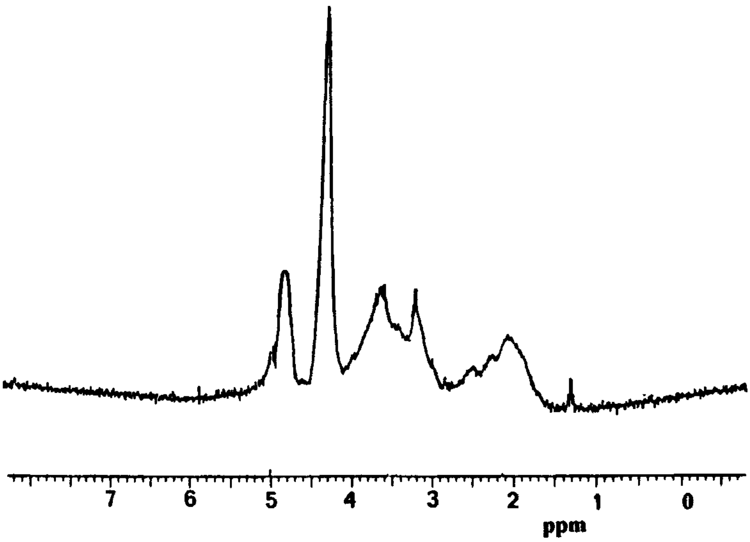


FIG. 2. $^1$H-NMR spectrum (250 MHz, $D_2O$, TMS as internal standard) of poly(acrylic acid-*co*-*N*-maleyl glycine), Sample 1.

AA), $\delta = 169$ ($-C{=}O$ of carboxylic acid), $\delta = 175$ ($-C{=}O$ of AA), $\delta = 177$-$180$ ($-C{=}O$ of imide) (see Fig. 3).

The poly(AAm-*co*-MG) was also synthesized by radical polymerization in dioxane at 70°C for 12 hours in the presence of AIBN. The results are summarized in Table 2.

The yields of the copolymers decreased with an increase of the monomer feed ratio of AAm. The yield of P(AAm-*co*-MG) copolymers were lower than those of P(AA-*co*-MG) copolymers. This could be explained by steric hindrance that favors the termination of chain transfer reactions during the P(AAm-*co*-MG) copolymerization. This could be attributed to the fact that the system acrylamide with MG has a lower rate of propagation than that with AA because of steric hindrance [14]. Steric hindrance in the imide of MG should also tend to slow propagation in favor of termination or chain transfer reactions, which would tend to give copolymers with lower molecular weights [15, 16].

FT-IR spectra of P(AAm-*co*-MG) showed strong absorption at $\nu$3500 $cm^{-1}$ (due to $-OH$ of $-COOH$), 2940 $cm^{-1}$ ($-CH$ of $-CH_2$ from MG), 1760 $cm^{-1}$ ($-C{=}O$ of imide), 1630 $cm^{-1}$ ($-C{=}O$ of amide), and at 1440 $cm^{-1}$ ($C{-}N$ of imide).

$^1$H-NMR spectra (250 MHz, $CD_3OD$, in ppm) show resonances at $\delta = 1.5$-$1.9$ ($-CH_2$ of AAm), at $\delta = 2.1$-$2.4$ ($-CH$ of AAm), at $\delta = 2.7$-$3.1$ ($-HC{-}CH-$ of MG), at $\delta = 4.2$-$4.3$ ($-CH_3COOH$), and at $\delta = 7.95$ ($-NHCO$).

## Determination of Monomer Reactivity Ratios

Reactivity ratios for the two copolymerizations were calculated by using the high-conversion method reported by Kelen-Tüdös [17]. The behavior of the systems

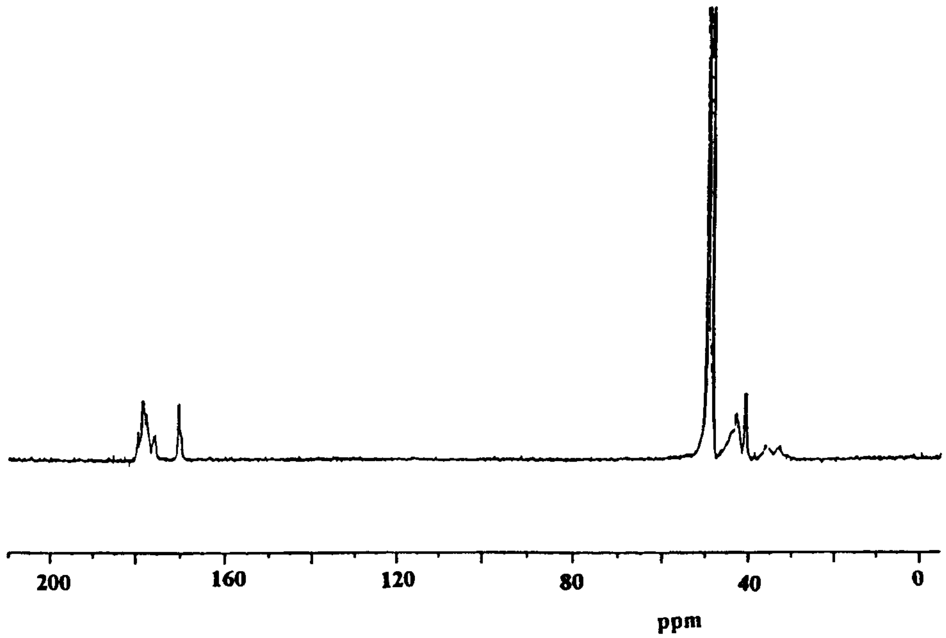


FIG. 3. $^{13}$C-NMR spectrum (62.9 MHz, $D_2O$, TMS as internal standard) of poly-(acrylic acid-*co*-*N*-maleyl glycine), Sample 1.

was evaluated through a plot of the copolymer composition ($F$) vs feed composition ($f$) (see Fig. 4).

The amount of bias depends on the actual values of $r_1$ and $r_2$, the extent of reaction, and the number of experimental points.

The Kelen–Tüdös equation symmetrically transforms into

$$G = r_1F - r_2 \tag{1}$$

by introducing the new parameters $\varepsilon$, $\eta$, and $\alpha = (F_{\min} \times F_{\max})^{0.5}$, where $F_{\min}$ and $F_{\max}$ represent the lowest and highest values of $F$ that are calculated.

TABLE 2. Experimental Data of the Radical Copolymerization of *N*-Maleyl Glycine (MG) with Acrylamide (AAm) at 70°C and 12 Hours in Dioxane

| Copolymer | $f$ | MG, mmol | AA, mmol | AIBN, mg | Solvent, mL | Yield, % | mp, °C | Copolymer composition,[a] MG:AAm |
|---|---|---|---|---|---|---|---|---|
| 1 | 0.50 | 0.7 | 0.7 | 2.1 | 1.0 | 46.8 | 220 | 0.50:0.50 |
| 2 | 0.75 | 1.0 | 0.3 | 2.1 | 1.0 | 33.4 | 270 | 0.65:0.35 |
| 3 | 0.90 | 1.3 | 0.1 | 2.4 | 1.0 | 32.0 | 300 | 0.82:0.18 |
| 4 | 0.25 | 0.3 | 1.0 | 2.1 | 1.0 | 58.4 | 320 | 0.40:0.60 |
| 5 | 0.10 | 0.3 | 2.9 | 5.3 | 2.4 | 64.0 | 310 | 0.20:0.80 |

[a] Determined from elemental analyses.

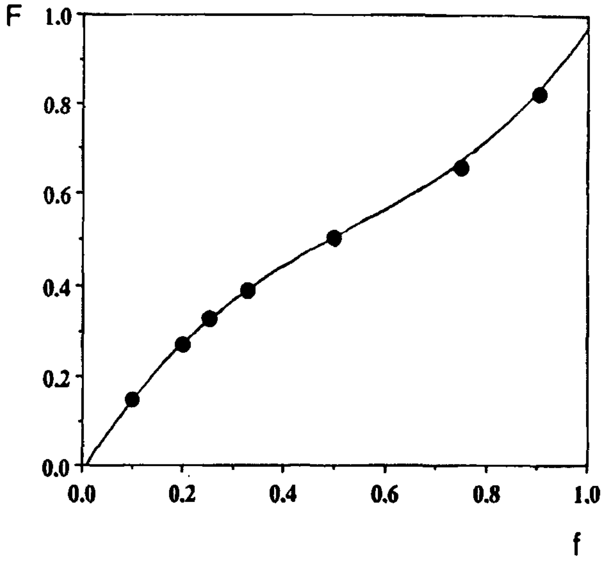


FIG. 4. Copolymerization composition curve of *N*-maleyl glycine with acrylic acid in dioxane at 70°C.

The transformed variables are defined as

$$\eta = G/(\alpha + F) \qquad \text{and} \qquad \varepsilon = F(\alpha + F) \tag{2}$$

where the variable $\varepsilon$ can take any possible value in the 0 to 1 interval. A plot of $\eta$ vs $\varepsilon$ gives a straight line, which on extrapolation to $\varepsilon = 0$ and $\varepsilon = 1$ gives $-r_2/\alpha$ and $r_1$, respectively (see Fig. 5).

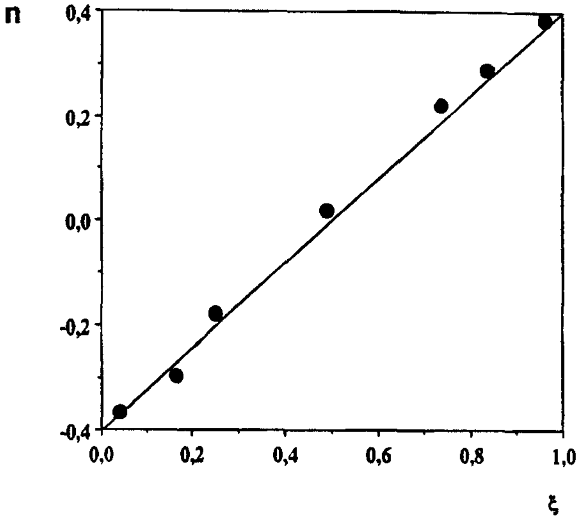


FIG. 5. $\eta$ vs $\varepsilon$ representation of the copolymerization parameters according to the K-T method for poly(acrylic acid-*co*-*N*-maleyl glycine).

Kelen–Tüdös modified this equation for high conversions by redefining $F$ and $G$ as follows:

$F = (m_1/m_2)/z^2$
$G = (m_1/m_2 - 1)/z$
Monomers (mmol) = $M_1$ = MG
$M_2$ = AA, AAm
Conversion, wt%
Polymer composition, mol%, $M_1 p_1$
$X_0 = M_1/M_2$
$y = p_1/(100 - p_1)$
$\delta_2 = W(\mu + X_0)/(\mu + y)/100$
$\delta_1 = \delta_2 y/X_0$
$z = \log(1 - \delta_1)/\log(1 - \delta_2)$
$F = y/z^2$
$G = (y - 1)/z$
$\alpha = (F_{\min} \times F_{\max})^{0.5}$
$\varepsilon = F/(\alpha + F)$
$\eta = G/(\alpha + F)$
$\mu = \mu_2/\mu_1$

$\mu_2$ and $\mu_1$ are the molecular weights of Monomer 2 and Monomer 1, respectively.

Copolymerization reactivity ratios were determined from consideration of feed monomer ratios of AA and AAm with *N*-maleyl glycine. The incorporation ratios were calculated from elemental analysis, giving best values for $r_1$ of 0.42 (MG) and $r_2$ = 0.40 (AA) and for P(AAm-*co*-MG) copolymers, $r_1$ = 0.27 (MG), $r_2$ = 0.30 (AAm).

Hocking et al. (15) applied the Kelen–Tüdös method and determined values of $r_1$ = 0.31 and $r_2$ = 0.55 for copolymerizations of sodium *N*-(4-sulfophenyl)maleimide (SPMI) with acrylamide. The copolymerization yield ranged between 1.5 and 16%, and decreased as the acrylamide in the feed decreased. Nevertheless, the copolymer showed a tendency to alternancy; acrylamide presented a higher tendency to homopropagate than copolymerization with *N*-maleyl glycine. This was

TABLE 3. Data to Determine the Reactivity Ratios for Poly(Acrylic Acid-*co*-*N*-Maleyl Glycine) [P(AA-*co*-MG)] Using the Kelen–Tüdös Method ($\eta$ vs $\varepsilon$, $\mu$ = 2.1528, $\alpha$ = 0.9669)

| $f$ | $M_1$ | $M_2$ | $W$ | $p_1$ | $\varepsilon$ | $\eta$ |
|---|---|---|---|---|---|---|
| 0.10 | 0.94 | 0.10 | 40.7 | 85 | 0.967 | 0.387 |
| 0.25 | 0.97 | 0.33 | 40.2 | 68 | 0.837 | 0.387 |
| 0.33 | 1.30 | 0.65 | 30.3 | 62 | 0.734 | 0.222 |
| 0.50 | 1.30 | 1.30 | 45.2 | 51 | 0.491 | 0.020 |
| 0.66 | 0.65 | 1.30 | 34.4 | 40 | 0.248 | −0.179 |
| 0.75 | 0.33 | 0.97 | 38.3 | 32 | 0.169 | −0.367 |

TABLE 4. Data to Determine the Reactivity Ratios for Poly(Acrylamide-*co*-*N*-Maleyl Glycine) [P(AAm-*co*-MG)] Using the Kelen–Tüdös Method ($\eta$ vs $\varepsilon$, $\mu = 2.1806$, $\alpha = 0.653$)

| $f$ | $M_1$ | $M_2$ | $W$ | $p_1$ | $\varepsilon$ | $\eta$ |
|---|---|---|---|---|---|---|
| 0.10 | 1.40 | 0.14 | 34.0 | 81 | 0.971 | 0.271 |
| 0.25 | 0.97 | 0.32 | 38.6 | 63 | 0.885 | 0.172 |
| 0.50 | 0.65 | 0.65 | 36.8 | 51 | 0.486 | 0.021 |
| 0.75 | 0.33 | 0.97 | 33.4 | 35 | 0.141 | −0.219 |
| 0.90 | 0.14 | 1.40 | 32.0 | 18 | 0.030 | −0.285 |

probably because SPMI would be expected to have a much lower rate of propagation than MG due to steric hindrance.

Results of the values $r_1$ and $r_2$ upon applying the Kelen–Tüdös method to the data of all copolymerizations are shown in Tables 3 and 4.

In both types of copolymers the monomers $M_1$ and $M_2$ have similar $r$ values; for example, P(MG-*co*-AA), K–T method, $r_1 = 0.42$; $r_2 = 0.40$. However, both $M_1$ and $M_2$ values are lower for the K–T method, and both copolymers show a tendency to alternation.

The Fineman–Ross method [18] was not employed as it is applicable only at very low monomer conversions.

## CONCLUSIONS

The yields of the copolymers P(AA-*co*-MG) and P(AA-*co*-MG) decreased as the feed monomer ratio of AA and AAm was increased. The yields of the copolymer P(AAm-*co*-MG) were lower than those of P(AA-*co*-MG).

The results of the two copolymerizations yielding P(AA-*co*-MG) and P(AA-*co*-MG) show that the monomers AA and AAm possess approximately the same reactivity toward MG. The low values of $r_1 \times r_2 = 0.168$ for P(AA-*co*-MG) and $r_1 \times r_2 = 0.081$ for P(AAm-*co*-MG) indicate that these copolymers have a strong tendency toward alternation.

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