Ethylene Copolymers of N-Substituted Acrylamides

GEORGE A. MORTIMER, *Monsanto Polymers and Petrochemicals Company, Texas City, Texas 77590*

Synopsis

Ethylene copolymers containing even small amounts of certain N-alkylacrylamides show some unusual properties: transparency while semicrystalline, preservation of stiffness during reduction in crystallinity, and an unusual melt flow-versus-solution viscosity relationship. These properties are due to hydrogen bonding between macromolecules. By proper choice of the N-alkyl group, copolymers containing more than 95% ethylene were made which were stiff, tough, and transparent.

INTRODUCTION

Studies in our laboratory on the effects of variation in molecular structure on the properties of low-density polyethylene have previously shown that bulky side groups introduced by copolymerization increase tensile strength and impact resistance, but with a corresponding decrease in stiffness.[1] We now report that copolymerization with small amounts of certain N-alkylacrylamides gives copolymers with increased tensile and impact strength with little or no loss of stiffness. Further, these copolymers are transparent.

EXPERIMENTAL

Copolymerizations where ethylene was the major monomer were carried out batchwise at 1360 atm and 130°C in a 240-cc vessel, as previously described,[1-3] using 14.4% propane as the chain transfer agent, which, for these monomers, kept almost all melt indexes between 1 and 6. The monomer mixture prior to polymerization was observed to be homogeneous in a high-pressure optical cell. Because of equipment designs, the polymerization itself could not be checked this way, so homogeneity or heterogeneity was inferred from toluene solubility. We had noted a similarity between the solvent power of toluene at 1 atm and ethylene at 1200–2500 atm in other work. In this work, if any polymer was formed which was insoluble in hot toluene, heterogeneity during polymerization was assumed and the run was not used. For example, this occurred above 6 mole-% N-isopropylacrylamide in the polymer but was not observed for diacetone acrylamide over the range studied. Data on the mole ratio of amide comonomer to ethylene in the reaction charge, expressed as per cent, is given for these two monomers in column 1 of Tables I and II.

TABLE I
Reactivity Ratio Data for Ethylene (M_1)-N-Isopropylacrylamide (M_2)[a]

M_2, mole-%		Calcd. M_2		Conversion,
In feed	In polymer	in polymer	Difference	wt-%
0.042	0.33	0.57	−0.24	2.4
0.123	0.94	1.75	−0.81	1.5
0.123	0.95	1.73	−0.78	1.6
0.122	0.91	1.74	−0.83	1.5
0.198	1.90	2.76	−0.86	1.7
0.247	2.09	2.40	−0.31	7.5
0.297	4.75	4.20	0.55	1.4
0.297	4.19	4.20	−0.01	1.4
0.398	5.39	5.32	0.07	2.2
0.398	5.53	5.55	−0.02	1.5
19.5	81.6	80.0	1.6	3.2
22.4	83.0	82.9	0.1	1.3
33.2	88.9	89.1	−0.2	6.0
35.8	89.6	89.8	−0.2	11.5
45.3	91.9	93.4	−1.5	0.3
45.3	91.9	93.4	−1.5	0.6

[a] $r_1 = 0.062 \pm 0.006$, $r_2 = 17.3 \pm 0.7$.

TABLE II
Reactivity Ratio Data for Ethylene (M_1)–Diacetone Acrylamide (M_2)[a]

M_2, mole-%		Calcd. M_2		Conversion,
In feed	In polymer	in polymer	Difference	wt-%
0.070	0.79	0.64	0.15	10.1
0.153	1.92	2.03	−0.11	5.2
0.224	3.43	3.24	0.19	4.1
0.307	3.83	3.27	0.56	8.4
0.391	5.83	5.53	0.30	4.3
0.523	6.76	6.70	0.06	5.8
0.608	8.14	6.72	1.42	8.3
0.767	7.20	9.88	−2.68	5.4
0.829	8.83	9.53	−0.70	7.6
0.866	12.8	10.4	2.4	6.6
1.07	12.6	11.5	1.1	9.0
1.13	10.3	11.2	−0.9	10.6
1.36	14.0	14.4	−0.4	8.7

[a] $r_1 = 0.047 \pm 0.010$, r_2 indeterminate.

To remove contamination prior to physical testing, each sample was dissolved in hot solvent, filtered hot, and precipitated with cold nonsolvent. Because the solubility characteristics of the copolymers changed with changing amide content, different solvent–nonsolvent pairs were used. Up to about 1.5 mole-% amide in the copolymer, toluene was the solvent and methanol the nonsolvent. At about 1.5 mole-% amide, this pair did not give complete precipitation, so an equal volume mixture of toluene and

dioxane was used as the solvent, and a 3:1 volume mixture of methanol and water was used as the nonsolvent. Following vacuum drying at 80°C, the samples were melt pressed into 20-mil slabs from which test specimens were die cut.

The tests used for physical and optical properties were either ASTM methods or modifications to permit smaller sample sizes, and all have been described elsewhere.[4-10] Copolymer compositions for the data of Table II were determined by elemental analysis for C, H, and N (Galbraith Laboratories). For each sample, the mole-% amide in the polymer was separately calculated from the H, the C, and the N values, and the three values were averaged to obtain the single value for the composition given in column 2. The difference between 100% weight and the sum of the wt-% C, H, and N should be O wt-% in the polymer. Although this value was not used in calculating the values in the table, it was used to calculate an approximate mole-% comonomer for comparison with the values from the C, H, and N analyses to ensure a reasonable material balance. If the four values were not in reasonable agreement, the sample was reanalyzed. This sort of care was required since the amount of comonomer was small. For example, the largest difference between calculated and measured values, 2.68 mole-% or 37 relative % for the eighth run in Table II, amounts to a difference of only 0.22 wt-% N which is within the range generally considered satisfactory agreement for elemental analysis.

[14]C-labeled N-isopropylacrylamide was used in the first ten runs of Table I, and scintillation counting was used to obtain the polymer composition since it was more precise than elemental analysis at low comonomer concentrations. In the last six runs of Table I, ^{14}C-labeled ethylene and unlabeled amide were copolymerized using a different procedure. Labeled amide was not used because of the difficulty of removing the last traces of amide monomer from the high-amide polymers. The 12th run in the table is illustrative of the procedure.

The same reactor was evacuated and a solution of 30.1 g N-isopropylacrylamide in 60 ml ethyl acetate was sucked in. The reactor was pressured with 25.9 g ethylene-^{14}C from a tared container. Into an inlet line separated from the reactor by a valve were placed 0.1 ml di-t-butyl peroxide and 0.5 ml benzene. The reactor was heated, with agitation, until the contents reached 130°C. Ethyl acetate was then pumped through the inlet line carrying the peroxide into the reactor and raising the pressure to 1360 atm within 4 min. After 45 min at an average temperature of 129°C, during which time ethyl acetate was added as required to maintain the pressure within ±2%, the reactor was carefully depressured and the contents drained into a large beaker. The reactor was washed with ethyl acetate and the wash combined with the reactor contents. The volatiles were removed on a rotary evaporator under vacuum, and the residue was purified by solution in acetone and precipitation with water. The polymer was then vacuum dried to yield 0.73 g (1.3% based on total weight of monomers) of a polymer which, by ^{14}C-scintillation counting, contained
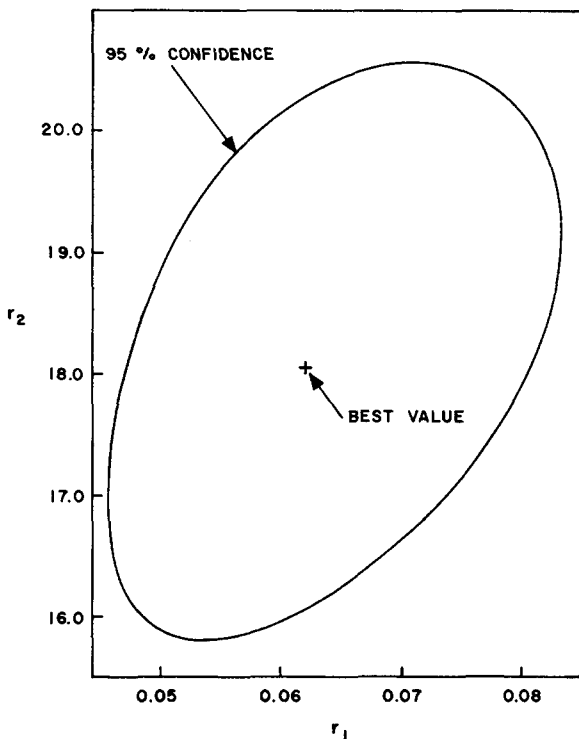
Fig. 1. Joint 95% confidence interval for ethylene (M_1)–N-isopropylacrylamide (M_2) copolymerization reactivity ratios from the data of Table I.

17.0 mole-% ethylene-^{14}C.   Runs with less than 80% amide in the polymer are not included in the table because the polymers were not completely soluble in ethyl acetate and heterogeneity during polymerization was suspected.

   Reactivity ratios were calculated from the data in Tables I and II by the nonlinear least-squares method of Tidwell and Mortimer,[11] integrating the copolymer equation.   The polymer compositions calculated from their $r_1 r_2$ values and the differences between the observed and calculated compositions are also given in the tables.   The differences do not appear to be completely random in Table I, suggesting that the copolymer model may not be exact for these data.   This might be due to the solvent change, analytical method change, or other factors.   The joint 95% confidence interval for r_1 and r_2 of the copolymer model (Fig. 1) is not abnormally large, suggesting that the copolymer model, even if not exact, is a reasonable approximation for most purposes.

RESULTS AND DISCUSSION

   Although a variety of acrylic and methacrylic amides were studied, this report will be limited to a discussion of the ethylene copolymers of two: N-isopropylacrylamide and N-1,1-dimethyl-3-butanonylacrylamide (re-
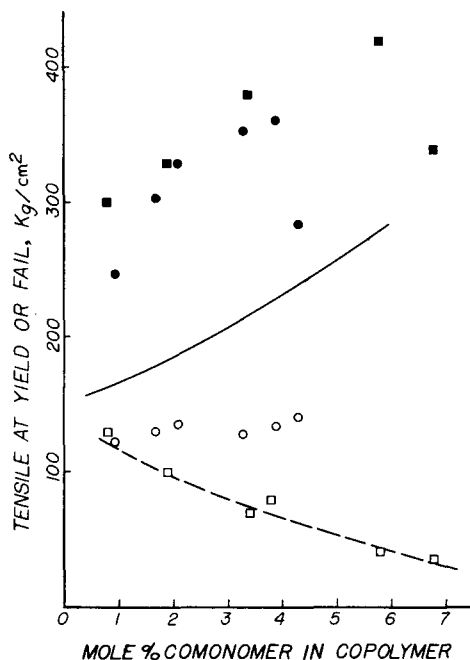
Fig. 2. Tensile strength as a function of copolymer composition. Open symbols are tensile at yield, filled symbols are tensile at fail. Dashed and solid lines are trend lines for tensile at yield and fail, respectively, for ethylene–vinyl acetate copolymers made under the same polymerization conditions. Circles are N-isopropylacrylamide and squares are diacetone acrylamide.

ferred to commercially and hereafter as diacetone acrylamide). These two have the advantages of being solids which do not polymerize during storage and yet are readily soluble in high-pressure ethylene over a relatively broad concentration range. These advantages assured that a homogeneous copolymerization reaction, free of contaminating homopolymers, could be obtained over a meaningful range of compositions. These two monomers illustrate the types of behavior found for all related monomers, so the specific behaviors of those not discussed can be estimated, qualitatively at least, from the general principles which will be set forth hereafter.

The copolymerization reactivity ratios for these monomers are in the same range as those reported for acrylate esters.[12] Thus, they depleted rapidly during polymerization and tended toward compositional heterogeneity, even at very low conversions, when used in low concentrations to give the "modified polyethylenes" of this study (see especially p. 439 in ref. 12). Different degrees of compositional heterogeneity would arise at the different conversions shown in Tables I and II and undoubtedly contributed to some of the scatter seen in the physical property measurements.

The tensile at fail and tensile impact data (Figs. 2 and 3) show that the isopropyl and diactone groups, as branched side chain moieties, con-
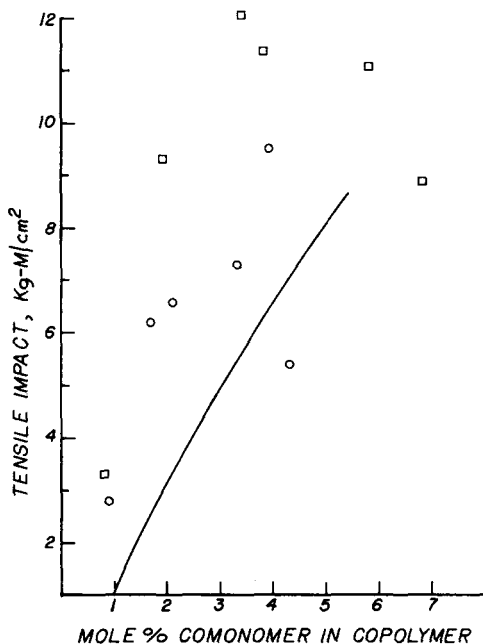
Fig. 3. Tensile impact as a function of copolymer composition.   Line and symbols refer to the same monomers as in Fig. 2.

tributed more toughness than the essentially linear acetoxy side chain moiety of vinyl acetate copolymers used as a reference for comparison. The very bulky diacetone moiety increased both tensile impact and tensile-at-fail values more than isopropyl, as expected from published correlations.[1] The same would undoubtedly be true of the corresponding esters.

The tensile-at-yield data (Fig. 2) show a unique property of these amide copolymers. Modulus data, not shown, displayed the same trend. Isopropylacrylamide copolymers did not lose stiffness as comonomer content increased. Diacetone acrylamide copolymers lost stiffness only as rapidly as the vinyl acetate copolymers, in spite of the side group being larger. The isopropylacrylamide copolymers could only retain their stiffness if another intermolecular binding force came into play in proportion to the reduction in interchain crystalline forces which certainly were being reduced by the comonomer side chains. The smaller-than-expected stiffness loss in the diacetone acrylamide copolymers must be similarly explained.

There is an indication in Figures 2 and 3, confirmed in further work[15] done with copolymers having a wider range of composition than covered in this study, that the tensile-at-fail and tensile impact values unexpectedly fall off at high comonomer concentration. With polyethylene, both of these measurements are strongly dependent on molecular weight, giving lower values as molecular weight decreases. Since all melt indexes on tested samples were in the range of 1 to 6, it had been assumed that molec-

TABLE III
Optical Data on 20-mil Slabs

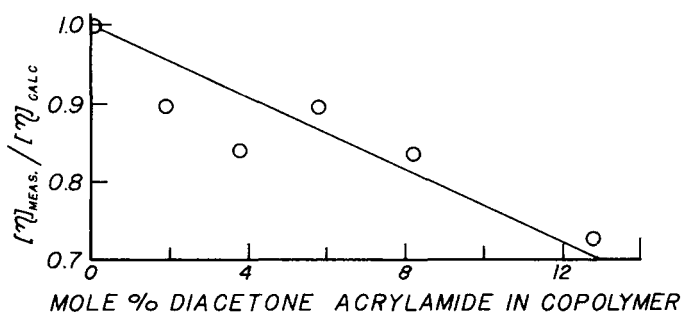| Comonomer	Mole-% in polymer	Haze, %	Transmission, %
Vinyl acetate	1.0	72	78
	4.7	49	80
Isopropylacrylamide	2.1	5	90
Diacetone acrylamide	0.8	66	72
	1.9	63	74
	3.4	6	84
	5.8	3	87
	6.8	3	87

Fig. 4. A measure of molecular weight reduction at constant melt index. Intrinsic viscosity measured in p-xylene at 105°C. Comparison calculated from measured melt index and $[\eta]$–M.I. relationship for polyethylene.[10]

ular weight was essentially constant. To check this assumption, the diacetone acrylamide content in the copolymer was plotted (Fig. 4) against the ratio of the measured intrinsic viscosity to the intrinsic viscosity calculated from the melt index using the relationship between the two developed for polyethylene.[10] The divergence from a ratio of 1.0 indicates the departure from the polyethylene correlation. Data for N-isopropylacrylamide copolymers showed the same trend. If the intrinsic viscosity is more nearly related to molecular weight than melt viscosity, which seems likely, then molecular weight was decreasing at constant melt index as comonomer content increased. This conclusion also fits polymerization results with corresponding acrylic esters where, as the amount of ester in the polymerization increased, copolymer melt index increased substantially.

The tensile-at-fail and tensile impact data are therefore explained as reflecting both comonomer and molecular weight effects. At low comonomer levels, the presence of bulky side chains brought about a large increase in toughness.[1] At higher comonomer levels, the substantially reduced molecular weight began to predominate.

Optical data, given in Table III, show that the amide copolymers became essentially transparent at lower comonomer contents than vinyl acetate copolymers. This cannot be explained by loss of crystallinity since

differential thermal analaysis indicated that crystallinity existed to roughly the same extent as for corresponding nontransparent vinyl acetate copolymers. The conclusion seems forced that the enhanced transparency is due to something keeping the spherulite size too small to scatter light.

It is postulated that the intermolecular force which enhanced stiffness, altered the melt-versus-solution viscosity relationship and kept spherulite size small is hydrogen bonding between amide groups. Interchain ionic bonding is known to produce the same set of property characteristics.[13,14] Two experimental facts make it quite conclusive that N–H hydrogen bonding is responsible for the unusual properties of these ethylene copolymers. First, infrared spectra of the solid copolymers as well as chloroform solutions showed hydrogen-bonded N–H and total absence of free N–H. Second, ethylene copolymers of N,N-dimethylmethacrylamide, where no N–H groups exist, showed none of these unusual properties.

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