Properties of Ethylene–Metal Acrylate Copolymers

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ABSTRACT: The dynamic mechanical properties of several ethylene–sodium acrylate and ethylene–magnesium acrylate copolymers have been investigated. The β transition temperature of the copolymers increase according to copolymerization theories. The monovalent salt copolymers exhibit a new transition above T_β which appears to arise from the breakdown of the secondary bonding network associated with the pendent salt groups. Melting points and crystallinities of all these copolymers are considerably below those of the original acid copolymers.

Polymers containing a small fraction of ionized, ionizable or highly polar pendent groups have been synthesized and investigated for a number of years. Primary efforts have been and continue to be directed toward rheological studies.

Beginning with Brown,[1] a large number of workers have studied the properties of amorphous carboxylic acid or carboxylate copolymers.[2–8] From these investigations have come a number of observations which may be summarized as follows.

1. In amorphous carboxylic acid copolymers, the formation of hydrogen bonded dimers is reversible above T_g. Below T_g the groups are immobilized within the glassy matrix. These dimers, which may form inter- or intramolecularly, are relatively inefficient above T_g when considered as permanent cross-links.

2. Carboxylate salts, while greatly increasing the glass temperature and generally stiffening the material in the rubbery plateau region, are also relatively inefficient and rheologically unstable when analyzed as cross-links. The structure and valency of the counterion has large effects on over-all material behavior.

Recently, interest has developed in such copolymers with ethylene, a crystallizable material as the major monomer. The added variable of crystallinity is a two-edged sword; unequivocal interpretation of rheological data is more difficult, but such systems offer an opportunity to study the crystallization behavior of copolymers. Studies on this system begin with those of Rees and Vaughn[9,10] and have been continued by several others.[11–14]

Papers on a wider scope which bear on the interpretation of behavior in polar copolymer systems include studies on polyacrylonitrile and its copolymers,[15–19] polyethylene oxide–salt complexes,[20] the systematic study of polyphosphates[21] and "polysalt" complexes.[22–24]

In the present study we will use ethylene–metal acrylate copolymers derived from ethylene–acrylic acid materials which have been characterized previously.[14] Conversions to the carboxylate form were carried essentially to completion to avoid the complications of having more than one type of interchain associative bonding present.

Experimental Section

Sodium and magnesium methoxides were freshly prepared by reacting the respective metals with anhydrous methanol. For the sodium salt the reaction was cooled while the magnesium reaction was carried out at room temperature.

The copolymers to be neutralized were dissolved in hot xylene (~1% solids), 1 drop of phenolphthalein was added and the base slowly added to the hot, stirred solution. This allowed much of the methanol to boil off, minimizing premature precipitation.

Actually, little precipitation occurred during the formation of the sodium salts. At the end point the hazy solution was kept hot for an additional 30 min, during which a 5% excess of methoxide was added. The solution was immediately taken down in 10 volumes of cold methanol, and the precipitate isolated by centrifugation. The fine solid was digested in hot methanol for several hours, filtered and dried under vacuum.

During the course of forming the magnesium salts, the copolymer separated from the hot solution in large gelatinous blobs. The gel was precipitated and dispersed in methanol with a high-speed blender. The fine precipitate was digested in a hot dilute magnesium methoxide solution for several hours, collected, washed with hot methanol and dried under vacuum.

The pressing of films for infrared examination and mechanical testing revealed large increases in the melt vis-

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Table I

Polymer	CH_3/ 100 CH_2	COO^-/ 100 CH_2	Density, g/cc
Na-B	~2.0	0.66	0.93
Na-C	~2.0	1.57	0.94
Na-D	<2.0 >1.5	2.26	0.96
Na-E	<2.0 >1.5	2.78	0.97
Mg-B	~2.0	0.66	~1.00
Mg-C	~2.0	1.57	>1.02

Table II

Polymer	T_m,[a] °C	T_c,[b] °C	Crystallinity, %
Na-B	99 ± 1	83 ± 2	24
Na-C	95 ± 2	68 ± 2	18
Na-D	93 ± 1	57 ± 2	11
Na-E	91 ± 1	49 ± 3	<5
Mg-B	95 ± 2	65 ± 2	18
Mg-C	92 ± 2	51 ± 3	<5

[a] Heating rate, 10°/min. [b] Cooling rate, 5°/min.

cosities of the copolymers. Where the acid copolymers were easily pressed at 130–140°, the sodium salts required 175–185° and the magnesium salts a minimum of 220°. In fact, films of only the two lowest members of this latter series could be prepared. The others were essentially infusible. An effort was made to carry out the neutralization in the solid state as reported by Fitzgerald and Nielsen[4] but incomplete reaction occurred.

Infrared analysis of thin films showed a minimum conversion of acid to salt of 90%. Therefore in Table I we report carboxylate content as equivalent to the original carboxylic acid content.

Melting points, crystallization points, and weight per cent crystallinities were determined on a Perkin-Elmer differential scanning calorimeter, D.S.C.-1B. Samples were melted, cooled at 5°/min and after 24 hr at 30° reheated at 10°/min. Data from this latter run were used for T_m and per cent crystallinity. Maximum departure from the base line was used for T_m. In other tests, samples were crystallized isothermally for 24 hr.

The dynamic mechanical properties of the carboxylate copolymers were measured on a Vibron instrument described elsewhere.[14]

Results and Discussion

The melting and crystallization temperatures and the crystallinities of the ionized copolymers are given in Table II In comparison with the original acid polymers,[14] we find sizable depressions in melting point and crystallinity, in line with the findings of others.[9,11,13]

One interesting feature of the behavior of the carboxylate copolymers is the increase in supercooling with increasing salt content. To make certain that the melting points reported are not artificially low because of low crystallization temperatures, samples were isothermally crystallized at low supercoolings, *i.e.*, ~10°. No significant (<1°) increase in the melting point resulted. This is an indication that the observed melting points are truly representative values. The data may be examined using Flory's copolymer crystallization equation[25]

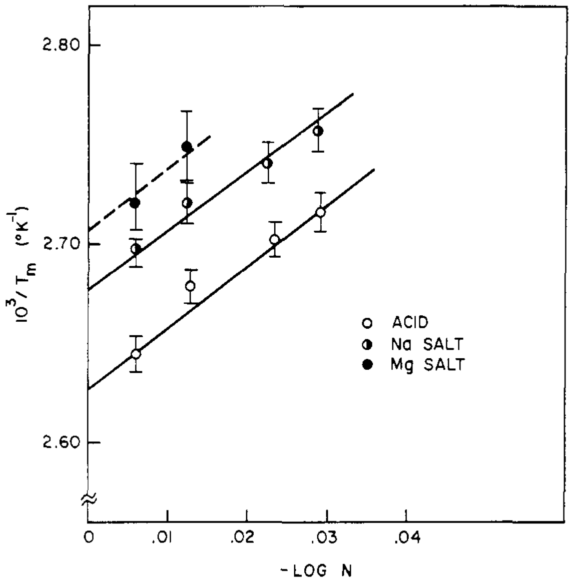

Figure 1. Flory plot of copolymer melting points.

$$\frac{1}{T_m} - \frac{1}{T_m^\circ} = -\frac{R}{\Delta H_u} \ln N \qquad (1)$$

where T_m = melting point of the copolymer, T_m° = melting point of homopolymer, $N \equiv$ fraction of crystallizable units, and ΔH_u is the heat of fusion of homopolymer crystals. The data are displayed in Figure 1 as $10^3/T_m$ *vs.* $-\ln N$. This gives $1/T_m^\circ$ as the intercept and $R/\Delta H_u$ as the slope. Also included for comparison are the data on the original acid copolymers.[14] The slopes of the lines are virtually the same giving ~755 cal/mol ($-CH_2-$) as the heat of fusion. This value is in good agreement with values obtained on other ethylene copolymers.[26] An important feature of the plot is that the extrapolated T_m°'s for the three systems are not the same. While little emphasis can be placed on the actual numerical values of T_m°, the trend of decreasing T_m° with increasing ionization and counterion valence cannot be overlooked. To examine more closely what this may mean on a molecular basis, the Hoffman–Lauritzen equation may be used[27]

$$T_m = T_m^\infty\left(1 - \frac{2\sigma}{\Delta H_u l}\right) \qquad (2)$$

where σ = fold surface free energy, l is the crystal thickness, and T_m^∞ is the melting point of a fully extended chain crystal. This equation is used to describe melting point depression in homopolymers as a function of crystal thickness. With the knowledge that both the acid[14] and salt groups are rejected from the ethylene crystals, however, we feel that this relationship may be used to the extent that it implies a discontinuous increase in the value of $2\sigma/l$ for the salt copolymers compared to the acid system. At this time it is not possible to determine which of these parameters is most altered. Electron microscope investigations of other workers[9,28]

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TABLE III

Polymer	T_β obsd, °C	T_β calcd, °C
Na-B	−14	−16.5
Na-C	−10	−11
Na-D	−5	−5
Na-E	−2	−4
Mg-B	−13	−14
Mg-C	−4	−7

show that the classical lamellar structure of spherulitic polyethylene, present in the acid copolymers, is essentially destroyed in the salt form. While this is only a qualitative observation, indications are of a decrease in the value of *l*.

The results of the dynamic mechanical tests on the sodium copolymer salts are shown in Figures 2 and 3. The individual data points have been omitted for clarity, but each curve is the result of at least 100 points.

Examination of the E'' or tan δ curves gives two striking results. The first is that what may be called the β transition temperature (−20 to 0°) increases with increasing salt content. The changes are much smaller than the increases in T_β brought about by the acid originally.[14] These observations generally agree with the findings of McKnight, *et al.*[12] The β transition temperatures for the sodium salt copolymers agree very well with the values predicted by the copolymerization equation $T_g = n_1T_{g_1} + n_2T_{g_2}$, where n is the mole fraction using 230° as the estimated glass temperature of poly(sodium acrylate). (The method of estimating the glass temperatures of the polymers of sodium and magnesium acrylate is described in Appendix I.) The observed and the calculated T_β values are listed in Table III and the agreement is excellent. Of further note is the observation that the intensity of the $E_{\max}''$ at T_β decreases linearly with the mole per cent of sodium acrylate in the amorphous phase (Figure 6) despite the large increase in the amorphous fraction of the material in going from sample B to E. Either the population of moving segments associated with this dispersion decreases regularly as the proportion of sodium acrylate increases, or the difference in mobility above and below T_β is decreased.

Furthermore, the regular shift of the β transition temperature argues strongly against a heterophase concept for these materials. The fact that the comonomer units are randomly distributed has been strongly suggested[29] and it now also appears that the salt groups are uniformly distributed on a molecular level.

The increase in the temperature of β relaxation with increasing salt content does not, by itself, rule out the formation of ionic domains. It may be argued, for example, that in fact that β relaxation arises from the motion of the amorphous ethylene sequence, with the increase in β temperature a result of constraints placed on this phase by the ionic domains which increase in size with increasing salt content. Furthermore, a decrease in the $E_{\max}''$ with increasing salt content is also expected from this model. However, it has been shown both experimentally and theoretically that the placement of a mechanical constraint on the amorphous ethylene region would result in a broadening of the E'' curve which was not observed in our results as salt content is increased. In addition, the agreement in the calculated and observed values of T_β appears to be more than a mere coincidence. Even if the aggregation of the salt groups exists to some extent, this does not necessitate a departure from the normal glass transition behavior of copolymers as long as the degree or the state of aggregation in the copolymer is no greater than in the ionic homopolymer.

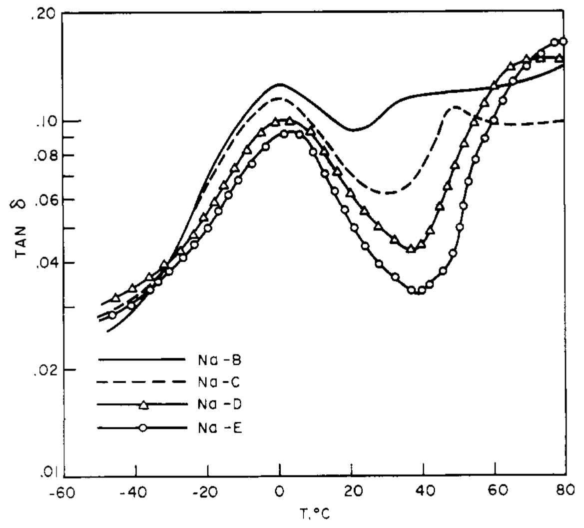

Figure 2. Loss tangents for sodium salt copolymers.

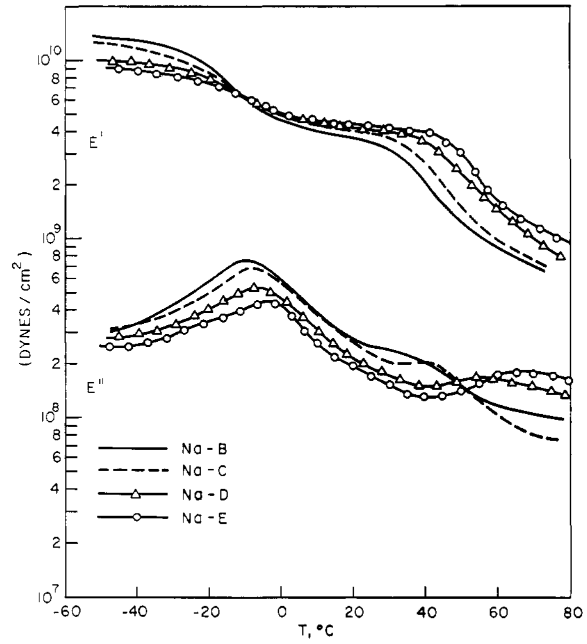

Figure 3. Dynamic mechanical data for sodium salt copolymers.

Another smaller but distinct loss peak appears to exist in these sodium acrylate copolymers in the region 40–80°. This dispersion cannot be considered the same as the α dispersion in linear PE because the temperature of the dispersion maximum increases with increasing salt content, contrary to the trend in melting points and degrees of crystallinity. The source of this loss dispersion may well be motions of larger segments of the polymer chain including the pendent sodium carboxyl-

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[29] I. Hopkins, personal communication.

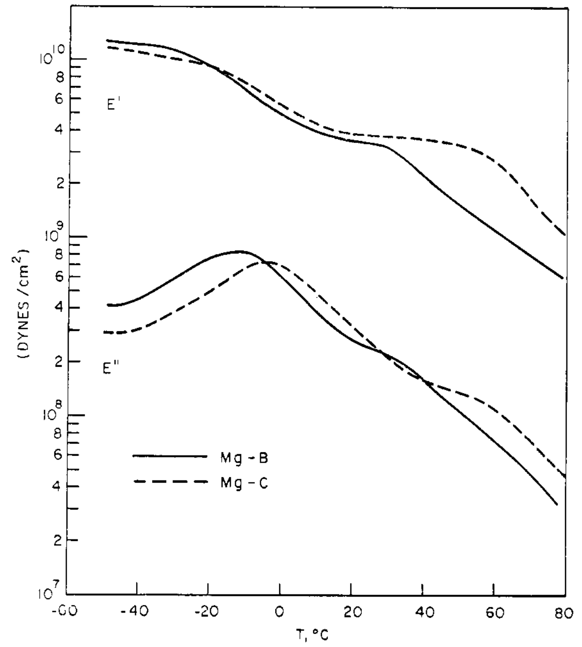

Figure 4. Dynamic mechanical data for magnesium salt copolymers.

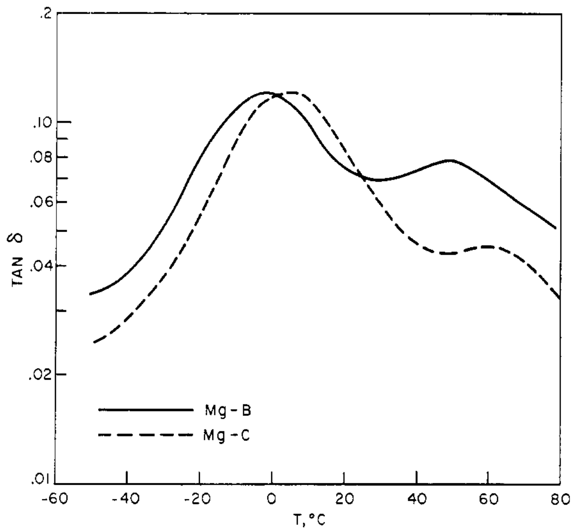

Figure 5. Loss tangents for magnesium salt copolymers.

ate group and may reflect the breakdown of the association between pendent salt groups. Similar interpretations have already been advanced.[11,30]

The elastic moduli E' of these copolymers are also shown in Figure 3. One interesting feature is that the E' values above T_β are higher for samples containing more sodium acrylate although the crystallinity decreases with increasing salt content. In sample E, the elastic modulus decreases so slowly with temperature in the range 20–50° that a plateau in the modulus–temperature curve appears to exist. This is in contrast with the data obtained in acrylic acid containing copolymers where the E' values above T_β decrease as the acid content increases and crystallinity decreases. Apparently, in these samples, the interaction of the sodium carboxylate groups outweighs the decrease in crystallinity and the sample is able to maintain a relatively high rigidity.

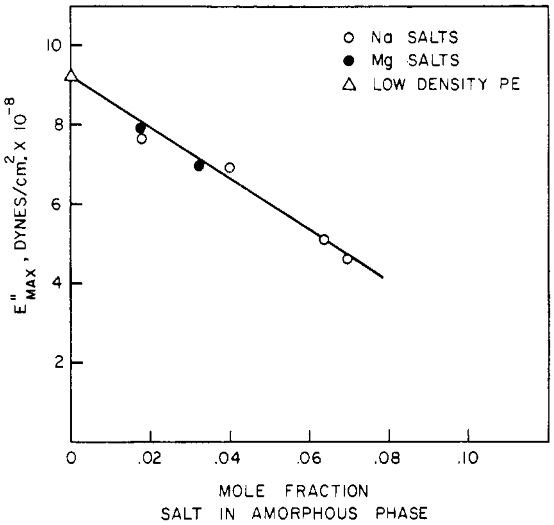

Figure 6. Loss modulus maximum as a function of the mole fraction of salt in the amorphous phase.

The elastic and loss moduli of the two Mg salt copolymers are shown in Figure 4 and the loss tangents are shown in Figure 5. Again the observed β transition temperatures are in good accord with the values calculated from copolymerization equation using 400° as the estimated T_g of poly(magnesium acrylate). Thus, the contribution of the monovalent Na salt and the divalent Mg salt to the increase in T_β of ethylene copolymers has the same underlying mechanism and can be accounted for satisfactorily by the composition of the copolymers. The $E_{\max}''$ value at T_β decreases with increasing mole per cent of magnesium salt, as in the case of sodium salt copolymers. Furthermore, the points lie on the same straight line representative of the data for sodium salt copolymers (Figure 6). (It is also of interest to note that the $E_{\max}''$ value of a low-density PE sample with comparable numbers of branches also falls on this line.)

Our mechanical data provide an indication that another small loss dispersion may be present in the temperature range 40–80° for these divalent salts. However, the elastic moduli of the magnesium salt copolymers above T_β are higher than the E' values of the corresponding sodium salt analogs and are larger than the E' values of any of the acrylic acid containing copolymers in this temperature region. In addition, the copolymer containing a larger percentage of magnesium acrylate maintains higher modulus at high temperature, although crystallinity of the sample has decreased below the levels in the sodium salt copolymers.

The source of the upper loss dispersion in the monovalent salts deserves additional comment and investigation. It appears as though the secondary bonding between these groups which imparts increased rigidity above T_β comes "unstuck" to a certain degree at the upper transition. If the interaction is of a primary ionic type, as put forth by Eisenberg for the polyphosphates, the transition temperature should vary with the *q*/*a* ratio of the cation. However, there is another type of interaction which seems possible in these more "dilute" ionic systems, that of dipole–dipole overlap.

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(30) W. J. McKnight, T. Kajiyama, and L. W. McKenna, *Polym. Preprints*, **9**, 534 (1968).

An investigation of dipole overlap thermodynamics is currently underway.

Conclusions

The general pattern of ionomer behavior reported by other investigators has been confirmed. Several additional factors may be added as a result of this work.

The first is that there appears to be a basic difference in the crystallization process when compared with the parent acid copolymers. The lack of correlation between the thermodynamic approach and polymer structural parameters leaves the nature of these differences in question.

The regular increase in T_β with salt content in agreement with a copolymer relationship suggests that the ionic groups are relatively uniformly dispersed through the amorphous material.

Finally, the upper transition in the monovalent salt copolymers moves upward with increasing salt content. Since the melting points decrease in the same sequence, it seems unlikely that the upper transition temperature is an α transition, but rather connected with the disruption of the secondary bonding network.

Appendix I

The procedure of estimating the glass temperatures of polymers of sodium and magnesium acrylate is as follows. First, the glass temperatures[4] of copolymers of styrene and sodium methacrylate or magnesium methacrylate were plotted as a function of the mole fraction of the salt and extrapolated linearly to obtain the glass temperatures of poly(sodium methacrylate) and poly(magnesium methacrylate) as 310° and about 490°, respectively. For the latter polymer, the extrapolation was made through only two points, the T_g of polystyrene and the T_g of one copolymer; thus the reliability of the estimated value was open to question. However, it appears that the glass temperatures of poly(methacrylic acid),[4] poly(sodium methacrylate), and poly(magnesium methacrylate) increase linearly with the charge-radius ratios (q/a) of the cations, as in the case of poly(phosphates). It is felt, therefore, that the estimated T_g values for the polymers of sodium and magnesium methacrylates are quite reasonable.

Second, it is assumed that the difference between the glass temperatures of poly(sodium acrylate) and poly(sodium methacrylate), or between poly(magnesium acrylate) and poly(magnesium methacrylate), is the same as that between poly(acrylic acid) and poly(methacrylic acid). This is equivalent to the assumption that the glass temperatures of poly(acrylic acid) and its salts have the same dependence on q/a as those of the poly(methacrylic acid) series. The estimated T_g of poly(sodium acrylate) is 230° and that of poly(magnesium acrylate) is 400°.

Composition of Graft Copolymers Formed by Electron Irradiation

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ABSTRACT: It is often desirable to ascertain the composition of a grafted copolymer system. For this work, vinyl monomers, acrylic acid and 1H,1H-dodecafluoroheptyl acrylate were cografted to an ethylene–propylene copolymer substrate. Providing that the grafted substrate does not act as a polymerizing material, and functions only as a source of free radicals, the classical copolymer composition equation may be used. Grafting was effected using a 250-kV electron beam accelerator. The influence of mutual solubility of the vinyl monomers on the calculated composition is also considered in this paper.

In the case of radiation-initiated grafting to an elastomer, it is often desirable to ascertain the composition of the product. It is expected that for a two-component comonomer system-to-elastomer graft, the well-known copolymer composition equation can be used directly, provided the following conditions or assumptions are valid: (1) transfer reactions and elastomer–elastomer addition reactions can be neglected, (2) the true monomer ratio in the polymer phase is used, and (3) during copolymerization there are no diffusion or phase change limitations.

The copolymer composition equation[1] is given as

$$\frac{\mathrm{d}m_1}{\mathrm{d}m_2} = \left(\frac{M_1}{M_2}\right)\left(\frac{r_1M_1 + M_2}{r_2M_2 + M_1}\right) \tag{1}$$

where $\mathrm{d}m_1/\mathrm{d}m_2$ is the ratio of monomer 1 to monomer 2 in the resulting terpolymer system; M_1 and M_2 represent the initial concentrations of the reacting solution; $r_1 = k_{11}/k_{12}$, the reactivity ratio of monomer 1; and $r_2 = k_{22}/k_{21}$, the reactivity ratio of monomer 2. However, should the monomers react with the substrate *via* an addition or transfer step, the copolymer composition equation would be modified as follows for the addition and transfer mechanisms.

addition mechanism

$$M_1\cdot + M_3 \xrightarrow{k_{13}} M_1M_3\cdot$$

$$M_2\cdot + M_3 \xrightarrow{k_{23}} M_2M_3\cdot$$

where $K_1 = (k_{23}/k_{22})M_3$ and $K_2 = (k_{13}/k_{11})M_3$

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(1) T. Alfrey, J. Bohrer, and H. Mark, "Copolymerization," Interscience Publishers, New York, N. Y., 1952, p 10.