Table V

Constants in eq 5	$r_{\eta 0}$	s
Present work	6	10
Ackers' work[a]	5	13

[a] See ref 33.

$$r_\eta = r_{\eta 0} + s\ \mathrm{erfc}^{-1}(K_d) \qquad (5)$$

The constant $r_{\eta 0}$ is the position of the maximum ordinate of the distribution, s the measure of standard deviation, and erfc^{-1} the inverse error function complement.

Ackers showed for several gels that a plot of r_η *vs.* $\mathrm{erfc}^{-1}(K_d)$ was linear and that $r_{\eta 0}$ and s could be taken to be calibration constants for a given gel. In present work, the available values of $K_d = (V_e - V_o)/V_i$ were graphed in terms of the inverse error function complement, $\mathrm{erfc}^{-1}(K_d)$,[34] *vs.* the corresponding estimated molecular radii, r_η, to yield the approximately linear relationship shown in Figure 8. Constants found for this line, together with those estimated from Figure 2 of Ackers' paper[33] are given in Table V. The proximity of $r_{\eta 0}$ and s values found in the present work with those reported by Ackers—although his plot is based on data from fractionation of dextrans—gives support to the above discussed concepts of the molecular size and the swelling relationships of NaLS molecules. Our experimental results seem to provide further evidence favoring Goring's interpretations as well as the present ideas concerning the mechanism of gel chromatography separations.

Acknowledgments. The authors appreciate the helpful counsel of Dr. Bjorn F. Hrutfiord of the College of Forestry and the Department of Chemical Engineering, and the substantial assistance given by Mr. Roger Wade of the Department of Biochemistry, of the University of Washington. They are also grateful to Dr. D. A. I. Goring of the Pulp and Paper Research Institute of Canada, and to Dr. Kaj Forss and Professor W. Jensen of the Finnish Pulp and Paper Research Institute of Helsinki for helpful discussions of their important work.

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[34] "Tables of the Error Function and Its Derivatives," National Bureau of Standards, Applied Mathematics Series 41, U. S. Government Printing Office, Washington, D. C., 1954.

Properties of Ethylene–Acrylic Acid Copolymers

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ABSTRACT: The effects of carboxylic acid comonomers on polyethylene are studied using calorimetry, dynamic mechanical testing, and infrared spectroscopy. Infrared studies indicate that the fraction of acid groups hydrogen bonded is determined by a temperature-dependent equilibrium with thermodynamic parameters similar to small molecule acids in ordinary solvents. During elongation, the planes of the acid dimer become perpendicular to the direction of stretch. The melting points of the copolymers are tested using Flory's equation. The results show that the acid groups are not crystallizable, and the dimerization takes place in the amorphous phase. The increases in T_g with increasing acid content as determined by E'' are more correctly described by cross-linking equations than by the simple copolymer relationships.

A variety of effects arise from the incorporation of comonomers with functional pendent groups in otherwise nonpolar vinyl polymers. In the cases of carboxylic acids, alcohols, amines, or amides, changes in physical properties are often identified with the hydrogen bonded structures formed. Systematic investigation of how relatively isolated functional groups alter polymer behavior is necessary in understanding the behavior of systems where they are major constituents.

Early investigations have shown that the presence of carboxylic acid or carboxylate comonomers generally increased matrix cohesion but did not lead to mechanically stable networks.[1-3] The picture of acid dimerization and acid–base interactions in amorphous polymers has more recently been refined. Below T_g the functional groups are highly associated and immobile. Above T_g chain mobility allows relatively free diffusion of the groups and the fraction associated is determined by a temperature-dependent equilibrium.[4-6] Superficially this latter behavior is identical with that of small molecule analogs in nonpolar solvents. The thermodynamic parameters of the association, however, may differ from the low molecular weight systems.

In this work the effects of acrylic acid comonomer on the properties of branched polyethylene are discussed where the additional variable of crystallinity is present. Several other authors have discussed such changes for the case of methacrylic acid and its metal salts. These experiments have shown that ionization of the acid depresses crystal formation more severely than does the

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(1) H. P. Brown (to B. F. Goodrich Co.), U. S. Patent 2,662,874 (1953).

(2) W. Cooper, *J. Polym. Sci.*, **28**, 195 (1958).

(3) W. E. Fitzgerald and L. Nielsen, *Proc. Roy. Soc.* (London), A282, 137 (1962).

(4) R. Longworth and H. Morawetz, *J. Polym. Sci.*, **29**, 307 (1958).

(5) E. P. Otocka and F. R. Eirich, *ibid.*, in press.

(6) E. P. Otocka and F. R. Eirich, *ibid.*, in press.

initial incorporation of the comonomer, yet stiffens the sample as a whole.[7–9] On the other hand, it is indicated that the β transition of the copolymers is raised more by the incorporation of the acid alone than by its univalent metal salt.[10]

Four ethylene–acrylic acid copolymers of varying composition were obtained from the Dow Chemical Co. and Union Carbide Corp. and the acid content was checked by titration. The methyl group content was determined by infrared analysis. These findings are summarized in Table I.

Experimental Section

Infrared Spectra. Three separate series of infrared experiments were carried out on the acid copolymers to determine the effects of composition, temperature, and elongation on their spectra. All data were taken on a Perkin-Elmer Model 21 prism instrument. For the elongation studies, a pair of Perkin-Elmer AgCl polarizers were employed.

Two special mounting techniques were used for the stretching and heating experiments. A steel frame was constructed to fit the spectrophotometer mounting slide. On this frame was a single screw, threaded in opposite directions on its upper and lower portions. As the screw is turned, the sample grips travelling on each threaded section move apart, allowing the midpoint of the film to remain in the center of the ir beam. Spectra were taken at a number of elongations to 200% with polarizations parallel and perpendicular to the direction of stretch.

A heated cell[11] was modified to allow study of the copolymer films above T_m without changes in thickness. The gas space of the existing design was eliminated and circular aluminum foil shims equal to the sample thickness were used as spacers. Circular samples were cut from the copolymer films to fit snugly within the area defined by the spacer. The sample and spacer were held by moderate mechanical pressure between salt plates during the experiments. Isothermal (±1°) scans of the 2–15-μ region were taken at about 10° intervals, and again during cooling. The intensities of the major bands of the spectra were virtually identical before and after heating.

Finally, series of three films of differing thickness from each copolymer were scanned to determine the extinction coefficient of one of the acid absorptions.

Calorimetry. The melting points and heats of fusion for the branched polyethylene reference and the four acid copolymers were determined on the Perkin-Elmer differential calorimeter, DSC-1B. The instrument was calibrated using the melting points of water and benzoic acid, 0 and 122°. Samples were cut from copolymer films, melted, then crystallized by cooling at 5.0°/min. After 24 hr at 25° the sample was remelted at 10°/min. The areas under the latter curves were determined by planimeter for crystallinity calculations. The maximum excursion from the base line was taken as the melting point. In a like manner, the maximum in the crystallization exotherm was taken as the crystallization temperature.

Solution Crystallization. Solutions of the copolymers in xylene (0.01% solids) were used in an effort to grow crystals from solution. While no single crystals could be obtained, all the samples yielded at least some very small, open, spherulitic crystal sheaths. Nucleation would not occur above 45° in this solvent, and the nucleation temperature was lowered to about 40° by the addition of 10% THF. Samples dissolved in tetradecane would nucleate at 75°, but only a few crystals would form at that temperature, with the remainder separating upon cooling.

TABLE I

PHYSICAL PROPERTIES OF ETHYLENE–ACRYLIC ACID COPOLYMERS

Polymer	Melt index	CH_3: $100CH_2$	COOH: $100CH_2$	Density, g/cc
A	2.0	3.5	0	0.918
B	4.8	~2.0	0.66	0.926
C	5.0	~2.0	1.57	0.935
D	4.8	>1.5 <2.0	2.26	0.946
E	6.9	>1.5 <2.0	2.78	0.953

Efforts to grow sizable spherulites in thin copolymer films bore out the unusually small dimensions of the crystalline regions in these materials. Even at 400× the birefringent areas appear only of pinhead size.

Mechanical Testing. The dynamic Young's moduli of the polymers were measured by a Vibron dynamic viscoelastometer[12] at a frequency of 110 cps, and over a range of −50 to +70°.

Results and Dicussion

Infrared. The thermal cycling of the acid-containing polymers was carried out to determine, if possible, the equilibrium constant for the acid dimerization, the ΔH for the dimerization (and therefore the ΔS), and the continuity of the association across the melting range.

There are a number of peaks in the infrared spectra of free and dimerized carboxylic acids which may be used to determine the amounts of each species present. The monomeric acid has an O–H stretching band at ~3540 cm^{-1} and C=O stretching at 1750 cm^{-1}.[13] The C=O stretch in the dimerized acid occurs at ~1705 cm^{-1}, with a molar (dimer) extinction coefficient almost exactly twice that of the 1750-cm^{-1} band. The ratio of these two bands has been used with more or less success by several workers[4,5,9] to determine the ratio of free and bound acid. Examination of the 1800–1650-cm^{-1} region of the spectra of the four acid copolymers on a Du Pont curve analyzer showed that four absorptions at 1750, 1735, 1705, and 1690 cm^{-1} were present in all samples at all temperatures. The interfering 1735-cm^{-1} band almost certainly represents polyethylene oxidation products, which are invariably present in high-pressure process materials. The intensity of the 1750-cm^{-1} (monomeric acid) absorption was very low at all but the highest temperatures investigated, indicating very effective dimerization. Reproducible exact synthesis of the total absorption curve was virtually impossible, and another method was sought.

Attention was directed to the use of the 940-cm^{-1} absorption which increases with acid content, and decreases with temperature. This absorption has been assigned to the out-of-plane O–H bending in the dimer.[14]

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(7) R. W. Rees and D. J. Vaughn, *Polym. Preprints*, **6**, 287 (1965).

(8) R. W. Rees and D. J. Vaughn, *ibid.*, **6**, 296 (1965).

(9) W. J. MacKnight, *et al.*, *J. Appl. Phys.*, **38**, 4208 (1967).

(10) W. J. MacKnight, *et al.*, *ibid.*, in press.

(11) M. G. Chan and W. L. Hawkins, *Polym. Eng. Sci.*, **7**, 264 (1967).

(12) M. Takayanagi, H. Harima, and Y. Iwata, *Mem. Fac. Eng., Kyushu Univ.*, **23**, 1 (1963).

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(14) D. Hadzi and N. Sheppard, *Proc. Roy. Soc.* (London), **A216**, 247 (1953).

Table II
Extinction Coefficients of Acid Dimers at 940 cm^{-1}

Polymer	Acid, mol/cc	ε, cm^2/mol
B	4.24×10^{-4}	3.58×10^4
C	9.71×10^{-4}	3.45×10^4
D	1.66×10^{-3}	3.52×10^4
E	2.00×10^{-3}	3.46×10^4

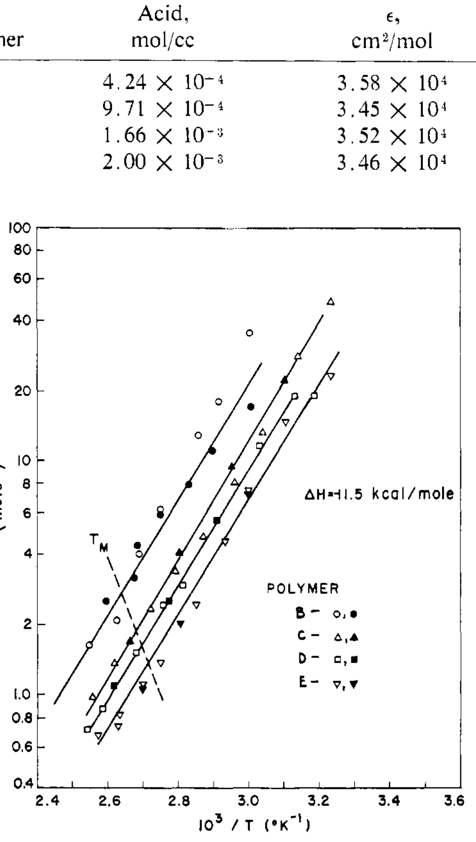

Figure 1. Association constants for the carboxylic acids in ethylene copolymers: ○, heating; ●, cooling.

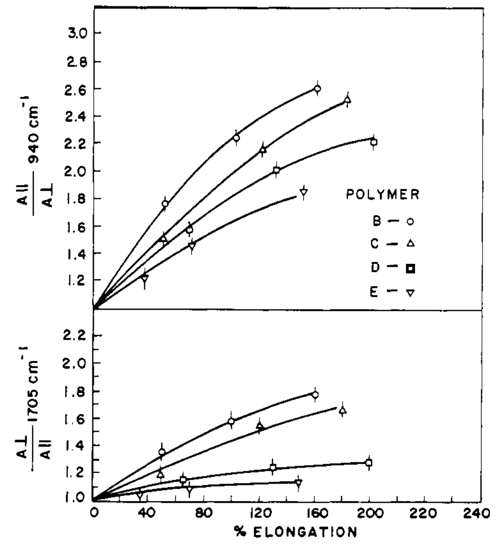

Figure 2. Dichroic ratios for the 940- and 1705-cm^{-1} absorptions as a function of elongation.

Samples of varying thickness of each of the copolymers were scanned in this region and extinction coefficients calculated from the known acid content on the assumption that dimerization was complete at room temperature. These results are shown in Table II. If the assumption was faulty, there should be a difference in the extinction coefficients from sample to sample. Since this is not the case, the data may be interpreted as an indication that about the same fraction of acid is associated in each sample at room temperature, and that this fraction is very close to 1.0. This agrees with the behavior of the 1750-cm^{-1} peak.

The 940-cm^{-1} absorption intensity was followed with temperature, and the results were used to calculate association constants, K_a. The K_a's for the four copolymers are shown in Figure 1.

The ΔH for dimer formation deduced from the slopes of the lines is -11.5 kcal/mol. This value is in excellent agreement with previously determined values for acid association in both polymeric and small molecule solvent media.[9,15] The ΔS per hydrogen bond for the four copolymers at 50° range from -12.5 to -11.3 eu with increasing acid content. These ΔS values in general agree with those observed in solutions of small molecule carboxylic acids.

An important feature of Figure 1 is the continuity of the bonding equilibrium through the melting region. This, along with the facile reversibility of the reaction, indicates that the bonding occurs within the amorphous region exclusively.

Finally, the dichroic ratios of the 940- and 1705-cm^{-1} absorptions were determined on thin films stretched stepwise to about 200%. Figure 2 shows that while the 1705-cm^{-1} absorption gives the expected weak perpendicular dichroism, the 940-cm^{-1} absorption is strongly polarized parallel to the direction of stretch. A space-filling model of the copolymer clearly explains this. If the ethylene chain is in an all-*trans* zigzag, which is highly favored during elongation, the acid side group rotation is blocked. The plane defined by the -C(=O)O of the acid must be roughly perpendicular to the plane defined by the backbone. The incorporation of two *gauche* conformations in the backbone allow free rotation, but this is energetically unfavorable. Thus, when the polymer chains are aligned, the dimer planes tend to be perpendicular to them and the out-of-plane transition moment is parallel to the direction of stretch.

The dichroic ratios for the 1705-cm^{-1} absorption are lower because of absorptions in the Z plane which do not register in this experiment. The trend for all dichroic ratios to decrease with higher acid content is at present unexplained, but could be a consequence of increased translational molecular motion because of the decrease in crystallinity (to be discussed below).

Calorimetry. The melting points and crystallization points are given in Table III. Also shown are the crystallinities of each sample, calculated from the heats of fusion and using 66 cal/g as the value for 100% crystalline polyethylene. While these transition temperatures are by no means ultimate or equilibrium values, they serve as a valid yardstick for comparison within the series.

The decreasing crystallinity with increasing acid content agrees with the trend reported by others[7,10] and with the observations of solution crystallization results mentioned earlier.

The melting points of the acid copolymers decrease

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(15) G. Pimentel and A. McClellan, "The Hydrogen Bond," Appendix A, W. H. Freeman and Co., San Francisco, Calif., 1960.

with increasing acid content. In the theory of Flory[16] the dependence of the melting point on the concentration of crystallizable units in a random copolymer is given by

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

where T_m is the copolymer melting point, T_m° that of the crystalline homopolymer, N is the mole fraction of crystallizable units in the copolymer, and ΔH_u the heat of fusion per mole of repeating homopolymer unit. In these copolymers, both methyl and carboxyl groups are present, and the proper choice of T_m° and N rests on the following considerations. It is known that the melting point depressions of polyethylenes with methyl, ethyl, and *n*-propyl substituents do not strictly follow Flory's equations.[17,18] The recent work of Holdsworth and Keller[19] shows that in crystallization from solution, chain folded lamellae can be grown from polyethylene containing sizable amounts of methyl and ethyl branches. Such branches are accommodated through less perfect packing and crystal habits. While crystallization from bulk may not make such generous allowances, it is highly probable that methyl groups are crystallizable to some extent, even in the bulk. Using, then, the branched polyethylene "A" as a reference for zero acid content, we should be able to test whether the acid units enter the crystal. As a first approximation we assume the acid groups are not crystallizable, and calculate N on the basis that all other units are crystallizable to the same extent as in polymer A. The results of this approach are shown in Figure 3. A straight line results, the slope of which gives a ΔH_u of 1510 cal/mol of ($-CH_2CH_2-$) or 755 cal/mol of ($-CH_2-$). This value, strictly speaking, is not the same as that of a methylene unit in an ethylene homopolymer because the reference point has been changed. Nevertheless, the magnitude compares favorably with the ΔH_u of 950 cal/mol ($-CH_2-$) (diluent method) and 925 cal/mol ($-CH_2-$) (calorimetric). The T_m° deduced from the intercept in Figure 3 is 108°, virtually the same as the melting point of sample A. The melting points and ΔH_u give a ΔS_u of about 2 cal/deg mol for these systems.

It is fully recognized that this application is not the way in which the equation was to be used. However, the apparent success of this approximation carries the strong implication that the acid units are not crystallizable and reside in the amorphous region of the copolymers.

TABLE III

DIFFERENTIAL SCANNING CALORIMETRY STUDIES

Polymer	T_m,[a] °C	Crystallinity, %	T_c,[b] °C
A	108 ± 1	40	90 ± 1
B	105 ± 1	40	87 ± 1
C	100 ± 1	35	85 ± 1
D	97 ± 1	21	80 ± 1
E	95 ± 1	16	77 ± 1

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

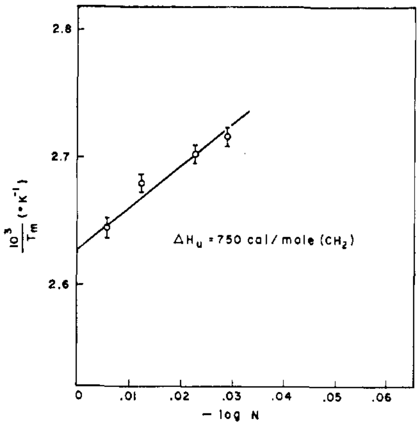

Figure 3. Melting point depressions of the copolymers.

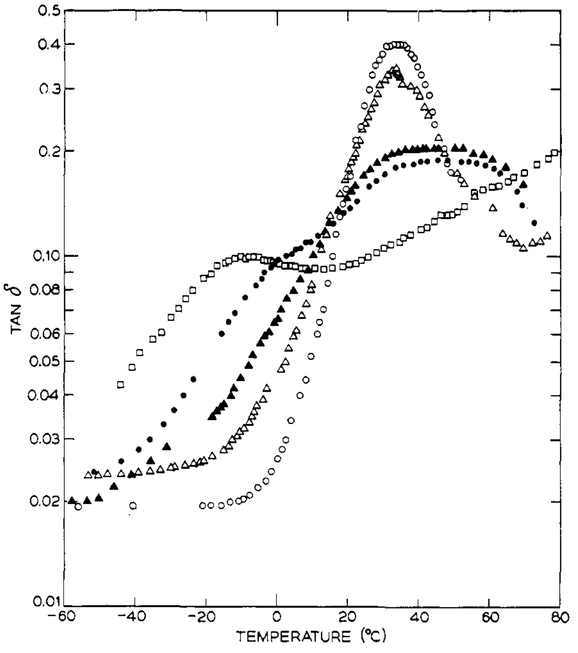

Figure 4. Loss tangents at 110 cps: □, polymer A; ●, B; ▲, C; △, D; ○, E.

Mechanical Testing. The loss tangent curves of the polymers are shown in Figure 4. The peak which occurs below 0° in the low-density PE can be identified as the β transition. On the other hand, the α transition (~80°) which is very pronounced in high-density PE cannot be easily located in the less crystalline polymer A. The tan δ curve for copolymer B containing 3 wt % acid shows a shoulder near 0° and then passes to a broad maximum at about 40°. We shall tentatively identify the shoulder as related to the β transition. It is not certain, however, whether the broad maximum at 40° has the same molecular mechanism as the α transition in high-density PE since the copolymer has about the same degree of crystallinity as the low-density PE. It appears that the interplay of two relaxation mechanisms prevents the clear separation of the loss peaks occurring near 0 and 40°. As the acid content increases, copolymer C shows only a broad maximum near 40° and copolymers D and E exhibit single sharp

(16) P. J. Flory, *J. Chem. Phys.*, **17**, 223 (1949).

(17) B. Ke, *J. Polym. Sci.*, **61**, 47 (1962).

(18) M. J. Richardson, P. J. Flory, and J. B. Jackson, *Polymer*, **4**, 221 (1963).

(19) P. J. Holdsworth and A. Keller, *J. Polym. Sci., Part B*, **5**, 605 (1967).

Table IV

Glass Transition Temperatures of the Copolymers

Polymer	T_g, °C	ΔT_g, °C	$\rho \times 10^3$, mol/cc
B	−5	16	0.38
C	12	33	0.80
D	20	41	1.10
E	24	45	1.24

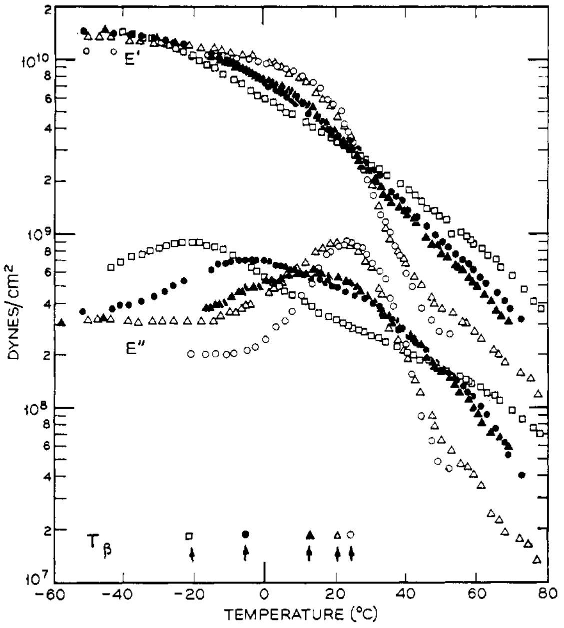

Figure 5. Dynamic elastic and loss moduli at 110 cps. Same symbols as in Figure 4.

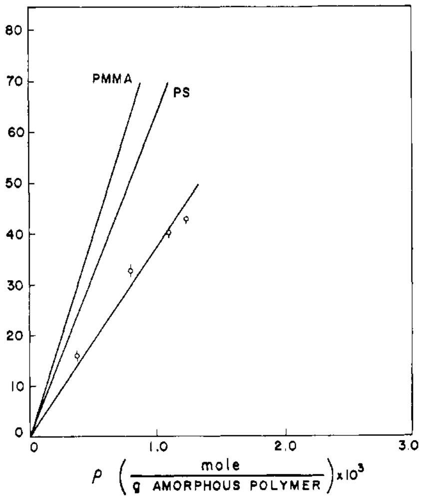

Figure 6. Change in glass temperature as a function of hydrogen bond cross-link density. ρ is expressed as moles of acid dimer per gram of amorphous polymer or as moles of covalent cross-link per gram of PS or PMMA.

loss peaks near 30°. Apparently in the latter two copolymers, one relaxation mechanism predominates.

The storage moduli E' of these materials are shown in Figure 5. As acid content increases and crystallinity decreases, the drop in modulus associated with the transition becomes more pronounced. It is also noted that, above 25°, the value of E' at a given temperature decreases as the crystallinity of the polymer decreases.

It is perhaps more appropriate to examine the loss dispersions of these low-crystallinity materials on the basis of loss modulus E''.[20] These curves are also shown in Figure 5. Well-defined loss maxima occur at −21, −5, 13, 20, and 24° for polymers A–E, respectively. The broad maxima in the tan δ curves of copolymers B and C near 40° now appear only as small, ill-defined shoulders (if they exist at all) in the loss modulus curves. In the ensuing discussion we shall direct our attention only to the well-defined maxima. Furthermore, we shall identify these loss dispersions as arising from segmental motions in the amorphous region, similar to the β transition in low-density polyethylene. These considerations are consistent with (1) the low degrees of crystallinity of these materials and (2) the observed rapid decrease in E' of copolymer D or E during the transition.

Since all four copolymers have approximately the same number of methyl branches as the low-density PE, the increase in T_g as one progresses from polymer A to the copolymer series may be attributed to acid content alone. The increase may arise from two possible contributions, the copolymerization effect and the cross-linking effect. In the first, since polyacrylic acid has a high T_g, namely, 106°, a copolymer of ethylene and acrylic acid is expected to have a higher T_g.[21] However, the copolymerization effect, as calculated for the amorphous phase from the equation of Gordon and Taylor,[22] gives estimated T_g values of −17, −13, −9, and −5° for the copolymer series. Therefore, it is not likely that the observed increase in T_g can be accounted for by the copolymer composition effect alone. In the second, the acrylic acid units existing mainly in the dimer form at room temperature may act as effective cross-links which restrict the motion of the backbone chain. In order to compare the observed increase in T_g with literature data on the effect of covalent cross-links on T_g, we calculate the cross-link density as follows: (1) all the acid units reside in the amorphous phase (based on melting point depression data), and (2) dimerization is essentially complete (based on ir results). The cross-link densities, ρ, expressed in moles per gram of *amorphous* material, and the increases in glass temperatures, ΔT_g, defined as [T_g(copolymer) − T_g(polymer A)] are listed in Table IV. A plot of ΔT_g *vs.* ρ gives a straight line as shown in Figure 6. The linear relationship between ΔT_g and ρ was derived by Fox and Loshaek[23] from a consideration of the volume shrinkage due to the formation of a covalent cross-link and was experimentally verified in cross-linked polystyrene[24] or poly(methyl methacrylate)[25] when the contribution to T_g by the copolymer composition effect of the cross-link was taken into consideration. (These data are also shown in Figure 6 for the purpose of comparison.) We

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(20) K. H. Illers and H. Breuer, *J. Colloid Sci.*, **18**, 1 (1963).

(21) L. A. Wood, *J. Polym. Sci.*, **28**, 319 (1958).

(22) M. Gordon and J. S. Taylor, *J. Appl. Chem.* (London), **2**, 493 (1952).

(23) T. G Fox and S. Loshaek, *J. Polym. Sci.*, **15**, 371 (1955 .

(24) K. Ueberreiter and G. Kanig, *J. Chem. Phys.*, **18**, 399 (1950).

(25) S. Loshaek, *J. Polym. Sci*, **15**, 391 (1955).

have not attempted to carry out a similar correction for the compositional contribution of the acid units to ΔT_g, because extensive dimerization of the carboxyl groups also exists in polyacrylic acid and it is impossible to assess independently the compositional effect. Even with these reservations in mind, it is still believed that the increase in T_g can be attributed mainly to the cross-linking effect, as implied by the agreement of our experimental data with the theory of Fox and Loshaek. The smaller proportionality constant between ΔT_g and ρ in our copolymers in comparison with that found for polystyrene or poly(methyl methacrylate) reflects the fact that volume shrinkage accompanying the dimerization of carboxyl groups is less than the volume decrease produced by the introduction of a covalent cross-link. Our results also fit the *empirical* equation of Shibayama and Suzuki[26] which are applicable to many covalently cross-linked polymers

$$T_g = K_1 \ln K_2\rho \qquad (2)$$

We therefore conclude that the dimerization of the acid units in these copolymers raises the T_g of a branched PE chain by a mechanism analogous to the action of covalent cross-links.

Once the T_β has been attained the segmental mobility allows the dimerization equilibrium to respond to thermodynamic control. Above this temperature the dimerization equilibrium is dynamic, *i.e.*, while the fraction of groups associated is specified by temperature, the identity of individual partners is lost. This means that interchange loss mechanisms are present at all temperatures above T_β. This view differs somewhat from that of McKnight, *et al.*[9] Additional evidence will be presented in a subsequent publication.

Conclusions

Three major conclusions may be drawn from the various experimental results.

The first is that the hydrogen bonding dimer formation is thermally reversible above room temperature, and probably above T_g. The thermodynamic parameters of the dimerization, namely, a ΔH of -11.5 kcal/mol and a ΔS of ~ -12 eu per H bond, are almost identical with the values for small molecule acids in nonpolar monomeric solvents. In addition, the monomer–dimer equilibrium is continuous through the melting temperature, implying that the bonding does not occur within crystalline regions. The application of Flory's equation confirms that the dimer formation occurs in the amorphous phase exclusively. These materials are good examples of severely restricted crystallization, showing an inability to generate sizable structures from solution or in bulk.

Within the amorphous phase, the presence of the dimers results in an increase of T_g. The dependence of T_g on acid content is more satisfactorily described by cross-linking equations than by comonomer equations.

Finally, under stress, where an all-*trans* backbone configuration is even more highly favored than at rest, the carboxylic acid side group is not allowed to undergo free rotation, and the dimers tend to lie perpendicular to the direction of stretch.

Acknowledgments. We wish to thank J. P. Luongo and B. Wargotz for their determination of methyl groups and acid content, respectively.

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(26) K. Shibayama and Y. Suzuki, *J. Polym. Sci., Part A*, **3**, 2637 (1965).

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p,p'-Biphenol–Dianilinosilane Condensation Copolymers[1]

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ABSTRACT: A series of linear polyaryloxysilanes having various combinations of methyl, phenyl, vinyl, and allyl substituents was synthesized by melt-condensing p,p'-biphenol and dianilinosilanes. These soluble thermoplastics were processable and exhibited potentially useful engineering properties at ambient temperature, but softened or fused at undesirable low temperatures, generally below about 100°. Cross-linked, insoluble polymers that softened, but did not melt, at 300° were obtained by free-radical cures of polyaryloxysilanes having pendent vinyl or allyl groups.

A wide variety of polymers based upon modified polysiloxane chains have been explored in recent years. Among these interesting new polymer types are the double-chain phenyl-T polymers,[2] the polysilazanes having silicon–nitrogen linkages,[3] polysilphenylenes in which silicon atoms are linked through phenylene

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(1) Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., Sept 10–15, 1965.

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