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

$$\frac{dm_1}{dm_2} = \left(\frac{M_1}{M_2}\right)\left(\frac{r_1M_1 + M_2}{r_2M_2 + M_1}\right) \qquad (1)$$

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

where dm_1/dm_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 $K_2 = (k_{13}/k_{11})M_3$

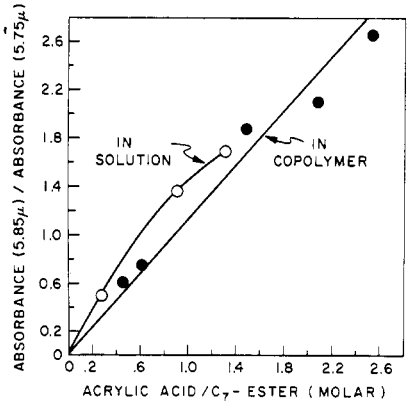

Figure 1. Ratio of absorbance of acrylic acid to absorbance of C_7 ester *vs.* molar ratio of acrylic acid to C_7 ester for monomer solutions and in copolymer.

transfer mechanism

$$M_1\cdot + M_3 \xrightarrow{k_t} M_1 + M_3\cdot$$

$$M_2\cdot + M_3 \xrightarrow{k_t} M_2 + M_3\cdot$$

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

$$\frac{dm_1}{dm_2} = \left(\frac{M_1}{M_2}\right)\frac{\left(\frac{M_1}{M_2} + \frac{1}{r_1} + \frac{K_2}{M_2}\right)\left(R\frac{M_1}{M_2} + \frac{RK_1}{M_2} + \frac{1}{r_2}\right)}{\left(1 + \frac{M_1}{M_2r_2} + \frac{K_1}{M_2}\right)\left(\frac{1}{r_1} + \frac{K_2}{M_2} + \frac{RM_1}{r_1M_2}\right)} \quad (2)$$

where $R = k_{31}/k_{32}$. Thus additional constants (*i.e.*, K_1, K_2) must be determined in this instance, and a knowledge of the copolymer composition alone is not sufficient. Note that if K_1 and K_2 become negligibly small, eq 2 reduces to the two-component eq 1. Since the elastomer substrate chosen for grafting does not contain residual unsaturation, only the possibility of a transfer mechanism will be considered.

Experimental Section

Materials. The substrate elastomer used for grafting was an ethylene–propylene copolymer (Enjay EPR 404) cured in slab form 0.070 in. thick using 3 pph of dicumyl peroxide, and heated for 25 min at 320°F. The monomers used were glacial acrylic acid (200 ppm of methylhydroquinone) and 1H,1H-dodecafluoroheptyl acrylate (C, ester) prepared by reaction of acryloyl chloride and the corresponding alcohol (Du Pont C_7 primary fluoro alcohol).

Procedure. Solutions of acrylic acid and the C_7 ester (in chloroform) were degassed and sealed *in vacuo* in small glass ampoules. Epr rubber samples were swollen in these solutions for 1 hr in a nitrogen atmosphere (<0.03% O_2). Samples were placed in radiation cells fitted with aluminum windows (0.0018 in. thick) and irradiated with 0.25 MeV electrons for a total dose of 184 Mrads, yielding grafts of less than 10% conversion of monomer. A dose of 1 Mrad corresponds to the absorption of 62.5×10^{18} eV/g of polymer. Samples were then extracted with acetone to remove soluble "homocopolymer," dried *in vacuo*, and examined by infrared spectroscopy.

Infrared Analysis. The surface of the rubber graft was analyzed using a Perkin-Elmer three-reflection attenuated total reflectance cell with a KRS-5 prism (ATR). A Perkin-Elmer Model 237 grafting spectrophotomer was used in conjunction with a Leeds and Northrup Speedomax H recorder to permit fivefold scale expansion of the appropriate portion of the transmission range. Since the acid and ester carbonyl absorbance characteristics are not necessarily the same for polymer as for monomer, the infrared system was calibrated for copolymer as well as monomer. Copolymer samples of known compositions were prepared based on the measured reactivity ratios of the monomers and calibrated against measured absorbance ratios of the acid peak (5.85 μ) to ester peak (5.75 μ). A similar calibration was performed for pure comonomer solutions. These calibration curves appear in Figure 1. The use of absorbance ratios compensates for any refractive index changes which might influence the depth of penetration in the ATR spectrum.

Table I

Fluorine, %	Molar ratios of acrylic acid to C_7 acrylate: In solution A/B	In copolymer a/b	Fineman and Ross functions: $F(1-f)$	F^2f
36.79	1.64	3.25	1.13	0.83
28.88	2.34	5.60	1.92	0.98
24.45	2.84	7.59	2.47	1.06
23.64	3.19	8.03	2.79	1.27

Reactivity Ratios

The reactivity ratios were measured by analyzing pure copolymer formed from a solution of acrylic acid and the C_7 ester. The comonomers, after degassing and sealing *in vacuo*, were carried to low conversion (<5%) by γ irradiation from Co^{60}. The copolymer formed was isolated, dried, and analyzed for per cent fluorine.

The molar ratio of acrylic acid to C_7 ester in the copolymer as measured by weight fraction fluorine in the copolymer is given by

$$a/b = 5.37\frac{1 - 1.695y}{1.695y} \quad (3)$$

where a/b is molar rato of acrylic acid to C_7 ester in copolymer and y is weight fraction of fluorine in copolymer. These data (Table I) were plotted using a Fineman and Ross plot[2] according to eq 4 (Figure 2)

$$F(1 - f) = r_1(F^2f) - r_2 \quad (4)$$

where $F = A/B$ is the molar ratio of acrylic acid to C_7 ester in solution and $f = b/a$, yielding reactivity ratios $r_1 = 3.8 \pm 0.6$, $r_2 = 1.8 \pm 0.3$. Error expected in r_1, r_2 data was based on precision obtainable from fluorine analysis.

In calculating reactivity ratios, the composition change of copolymer is neglected at low conversions. In order to justify this simplification, one can examine the ratio of instantaneous composition to the average accumulative composition. It is copolymer having an average accumulated composition that is measured experimentally. Utilizing the approach of Skeist,[3] one can calculate for a given set of reactivity ratios both the instantaneous and accumulative compositions. Equations 5 and 6 are used for these calculations,

(2) M. Fineman and S. Ross, *J. Polym. Sci.*, **5**, 269 (1950).
(3) I. Skeist, *J. Amer. Chem. Soc.*, **68**, 1781 (1946).

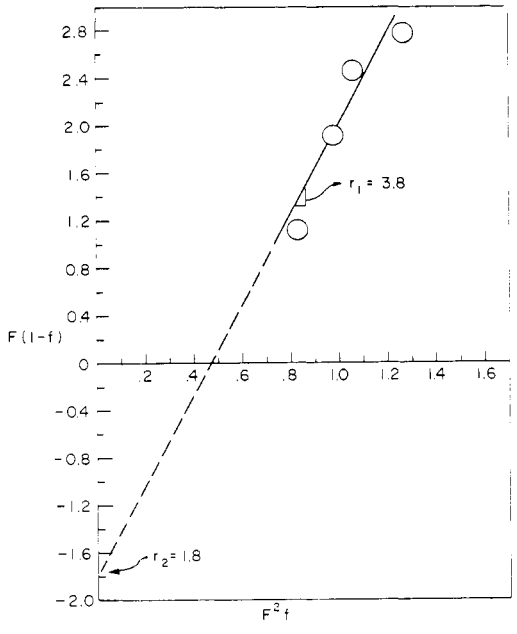

Figure 2. Fineman and Ross plot: monomer 1 is acrylic acid, monomer 2 is C_7 ester, $r_1 = 3.8$, $r_2 = 1.8$.

$$\ln (1 - \alpha_p) = \int_{A_0}^{A_f} \frac{dA}{a - A} \tag{5}$$

$$\alpha_A = \frac{A^0 - (1 - \alpha_p)A_f}{\alpha_p} \tag{6}$$

where α_p is the over-all conversion of total monomer to copolymer, A_0 is the initial mole fraction of acrylic acid in solution, A_f is the final mole fraction of acrylic acid in solution, A is the mole fraction of acrylic acid in solution, a is the mole fraction of acrylic acid in copolymer at any moment, α_A is the average accumulative composition of acrylic acid in the copolymer, and α_i is calculated from the copolymer composition equation for the instant the concentration is given by A. The integral was evaluated using Simpson's rule through the use of a General Electric 235 time-sharing computer.

The calculated data from these relationships (Table II) clearly indicate that for up to 10% conversion of monomer to copolymer, the instantaneous composition is virtually identical with the accumulative composition for the experimentally measured reactivity ratios, and in the concentration range used. Skeist points out that this property of homogeneity is a function of both the reactivity ratios and the initial concentrations.

In the vast majority of cases encountered in the literature, the product of the reactivity ratios, r_1,r_2, is less

TABLE II
CONVERSION OF INSTANTANEOUS AND ACCUMULATIVE MOLE FRACTION AT 10% CONVERSION TO POLYMER

A_0	α_i	α_A	α_A/α_i
0.60	0.7337	0.7435	1.013
0.65	0.7882	0.7962	1.010
0.70	0.8360	0.8420	1.007
0.75	0.8735	0.8810	1.008
0.80	0.9125	0.9125	1.000

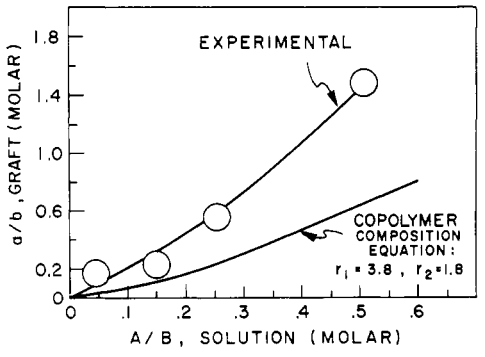

Figure 3. Ratio of acrylic acid to C_7 ester in graft copolymer *vs.* initial molar ratio of acrylic acid to C_7 ester in the swelling solution.

than 1; however, the r_1,r_2 product in our case is greater than one ($r_1r_2 = 7.2$). This indicates that acrylic acid and the C_7 ester monomers selectively add to their own type of radical, resulting in the block copolymer structure —baaaabbbbaaabbbaaab—. Several such systems have been reported in the literature[4–7] and are taken to be only an indication that blocking of monomers can occur.

Furthermore, in applying the γ-ray measured reactivity ratios to electron beam initiated graft structures, it is assumed that only the rate of grafting is influenced by the high dose rate and no effect on copolymer composition occurs.

Results

The measured ratios of acrylic acid to C_7 ester found in the graft system are plotted (Figure 3) as a function of the monomer ratio of the initial graft solution. The lower curve represents the composition predicted by the copolymer composition equation. Experimental results indicate a higher fraction of grafted acrylic acid than predicted, suggesting perhaps that the acrylic acid monomer is more soluble in the rubber than the C_7 ester or perhaps a chain-transfer mechanism is influencing the observed graft composition. Empirically derived constants for R, K_1 and K_2 for eq 2 (*i.e.*, $R = 12$, $K_1 = 0.1$, $K_2 = 3.0$) lead to the conclusion that acrylic acid would need a chain-transfer constant 30 times greater than that of the C_7 ester, a highly unreasonable conclusion. Therefore, our approach was to investigate possible concentration variations.

To establish the actual concentrations of the monomers swollen in the epr rubber, several samples were placed in known concentrations of monomer for 1 hr, removed and the surface was analyzed by ATR infrared for the ratio of acrylic acid to C_7 ester. These data are plotted (Figure 4) as A/B in the epr *vs.* A/B in the solution.

When the measured composition of the graft product is plotted (Figure 5) as a function of A/B *in* the epr, it is found that the copolymer composition equation indeed is applicable.

(4) J. Brondrup, *Faserforsch. Textiltech.*, **12**, 135 (1961).
(5) H. Tatemichi, and S. Suzuki, *Kogyo Kagaku Zasshi*, **63**, 1843 (1960); *Chem. Abstr.*, **56**, 13084 (1962).
(6) T. Kimura and K. Yosheda, *Kagaku To Kogyo* (Osaka), **32**, 223 (1958); *Chem. Abstr.*, **53**, 4806 (1959).
(7) T. Tomikado and Y. Iwakura, *J. Polym. Sci.*, **36**, 529 (1959).

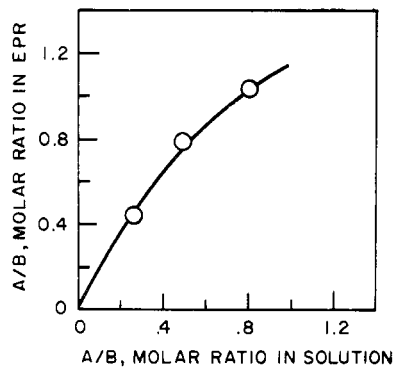

Figure 4. Equilibrium ratio of acrylic acid monomer to C_7 ester monomer which actually is contained in epr *vs.* ratio of acrylic acid monomer to C_7 ester monomer in the swelling solution.

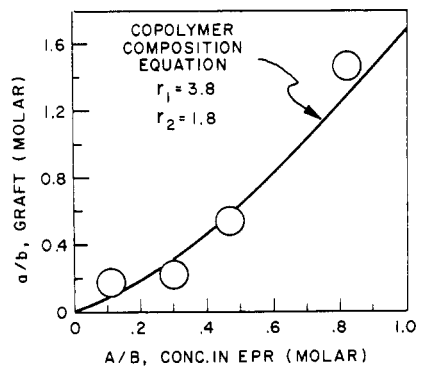

Figure 5. Ratio of acrylic acid to C_7 ester in graft copolymer *vs.* ratio of acrylic acid monomer to C_7 ester monomer actually contained in the epr.

Conclusions

Our results indicate that, aside from the polar influences or steric effects described by Odian and coworkers,[8] the composition of a graft formed from a substrate swollen by a comonomer solution may be predicted by the two-component copolymer composition equation.

Acknowledgment. The authors take pleasure in acknowledging Mr. John Parsons for his valuable assistance in the use and calibrations of the attenuated total reflectance infrared system used for this study.

(8) G. C. Odian, A. Rossi, and E. N. Trachtenberg, *J. Polym. Sci.*, **42**, 140 (1960).

The Role of Hydrogen Bonding in the Photochemistry of Poly(*t*-butyl N-vinylcarbamate)

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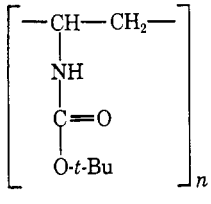
ABSTRACT: The quantum yield (ϕ_{II}) for cycloelimination of isobutene and CO_2 from thin films of poly(*t*-butyl N-vinylcarbamate) was found to be 0.01. In contrast, quantum yields in alcoholic solvents were 0.04 and hydrocarbon media gave values of 0.16. From the solvent shifts of the electronic spectra and approximate phosphorescence lifetimes, the lowest reactive excited state of the polymer in hydrocarbon solvents was deduced to be of $n-\pi^*$ character while in alcoholic solvents and film form a carbonyl $\pi-\pi^*$ excited state abstracted the β-ester proton. It was found that intermolecular hydrogen bonding (N–H···O=C) of the *gauche* rotamer of the ester moiety played a significant role in reducing the quantum yield in thin films. Evidence for this was gained from solution and thin film infrared spectra data analyzed relative to the temperature dependence of the cycloelimination quantum yield.

Previous studies[1] on the solid-state photochemistry of poly(*t*-butyl acrylate) have shown that the primary process is a Norrish type II elimination yielding isobutene and poly(acrylic acid). In addition, the photoreaction was found to take place from an $n-\pi^*$ state of the carbonyl group.[1b] Another aspect of the previous work was that a photoinduced rotational isomerization occurred between the *cis* and *gauche* forms of the ester with subsequent cycloelimination from the *cis* rotamer. The present study pertains to a relationship between the photochemical and spectroscopic properties of poly(*t*-butyl N-vinylcarbamate). Comparative experiments were made with poly(*t*-butyl acrylate) to understand better the effect of the amino group between the polymer backbone and ester group. Particular emphasis was given to details of the nature of the excited states involved and intermolecular bonding of the carbamate (CO–NH) group to rationalize differences between the polycarbamate and polyacrylate



(1) (a) A. R. Monahan, *J. Polym. Sci., Part A-1*, **4**, 2381 (1966); (b) *ibid.*, **5**, 2333 (1967).