JOURNAL OF APPLIED POLYMER SCIENCE VOL. 16, PP. 3017–3034 (1972)

Terpolymers. I. The Mechanical Properties and Transition Temperatures of Terpolymers of *n*-Octadecyl Acrylate, Ethyl Acrylate, and Acrylonitrile

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Synopsis

Earlier work revealed that the internal plasticization of polyacrylonitrile by the higher *n*-alkyl acrylates or N-*n*-alkylacrylamides yielded only brittle copolymers. This difficulty was circumvented in the present work by starting with copolymers of acrylonitrile and ethyl acrylate, over the range of compositions, and further modifying these by incrementally displacing the ethyl acrylate in each recipe by *n*-octadecyl acrylate through terpolymerization. In this way, the stepwise small reduction in T_g for the base ethyl acrylate–acrylonitrile copolymers was greatly increased for each of the terpolymers. Compositions were obtained ranging from glassy, brittle terpolymers, with glass transitions above room temperature, to soft plasticized polymers having sufficient polar networks retained from the nitrile to confer useful properties. The decline in the glass temperature was shown to be dependent on the free volume conferred by the side-chain methylene groups of each acrylate ester. In contrast, the decline in tensile and flexural strengths and moduli for the terpolymers having glass transitions above room temperature was produced entirely by the presence of the methylene groups of the 18-carbon ester. The glass transition region corresponded to room temperature when the acrylonitrile content of the base copolymer had been reduced to 50 mole-%. Terpolymers of this nitrile content and lower had the low moduli and large elongations of plasticized compositions. An equation was developed which correlated empirically the glass transitions and the mechanical properties with the weight fraction of the acrylate esters for the glassy terpolymers.

INTRODUCTION

Vinyl comonomers, with long linear side chains and derived from animal fat, have not always been equally effective in internally plasticizing brittle homopolymers having high glass transition temperatures or levels of crystallinity. While vinyl chloride was readily plasticized by vinyl stearate[1] and vinylidene chloride by *n*-octadecyl acrylate and certain N-*n*-alkylacrylamides,[2,3] predominately brittle compositions resulted from incorporating long side-chain *n*-alkyl acrylates[4] and N-*n*-alkylacrylamides[5] into

polyacrylonitrile. Polyacrylonitrile might be unusual, however, because of the special properties conferred by its microstructure.[6a] Intramolecular dipole repulsions of the cyano group[7] prevent crystal ordering in the chain direction[8] while enhancing lateral order through strong intermolecular hydrogen bonding.[6b] This order can persist undisturbed in copolymers, even those containing as much as 20 mole-% of a randomly distributed comonomer.[9] The residual order might even contribute to the maxima or minima found in T_g–composition curves for certain copolymers.[6c] In view of the peculiar conformational restrictions and electrostatic interactions of polyacrylonitrile, two glass transitions have been postulated[10] to help explain the uncertainty regarding a variety of reported glass transition temperatures for the homopolymer.[6c,7,11] A glass transition occurring at 87°C was attributed[10] to intermolecular Van der Waal's forces, while another at 140°C was presumed to be caused by dipole–dipole associations between chains, leading to semipermanent networks. The generally accepted T_g is[12] 105°C and can be considered to be an average of the two transitions. Thus, the effect on properties conferred by long side-chain molecules in copolymers with acrylonitrile is not readily predictable and may appear to be anomalous.

On the other hand, the marked efficiency of these long side-chain esters, especially the 18-carbon comonomers, in lowering the flex temperature of brittle polymers is well established.[1–3] However, a recent study[13] of the internal plasticization of poly(methyl methacrylate), which has a glass transition (105°C) similar to that of polyacrylonitrile, by the *n*-alkyl acrylates and N-*n*-alkylacrylamides gave results relevant to the work on acrylonitrile systems. In this study, the mechanical properties declined to impractically low levels even before the glass transition reached room temperature, giving rise to generally brittle compositions. Additive contributions to the free volume made by each side-chain methylene group to the glassy matrix were shown to be responsible for the results observed. Conceivably, a similar phenomenon may occur in the acrylonitrile copolymers[4,5] even though they possess a polar network microstructure. If this is the case, the high glass transition temperature of polyacrylonitrile might conceivably be lowered by incorporating a nonplasticizing comonomer, but one whose homopolymer possesses a lower T_g, to yield a base copolymer system. The base copolymers could then be efficiently plasticized by including a fatty comonomer in the polymerization recipe as a third component. Thus, ethyl acrylate could be the T_g modifier and *n*-octadecyl acrylate would serve as the internal plasticizer. In this way, the polar network contributed by the acrylonitrile could be largely retained while thermoplastic compositions of low modulus should result. This would obviate the requirement of vulcanization and the use of fillers needed to introduce adequate mechanical properties into soft copolymers of the lower acrylate esters having only small inclusions of acrylonitrile.[14,15]

In this investigation sets of mole fraction combinations of acrylonitrile and ethyl acrylate, across the range of composition, were in turn modified

by incrementally replacing the ethyl acrylate by *n*-octadecyl acrylate in each set. Mechanical properties were correlated with the glass transitions for all terpolymers. The free-volume contribution to these properties was estimated for each side-chain methylene group. Increased moduli, resulting from side-chain crystallinity which developed as the *n*-octadecyl acrylate content was increased beyond a critical amount, were interpreted in view of recent studies of side-chain crystallinity in copolymers[16,17] and in homopolymers.[18]

EXPERIMENTAL

Monomer Preparation

Acrylonitrile and ethyl acrylate were the purest available from commercial sources. The nitrile was fractionally distilled through a short-lagged Widmer column, and a middle cut, boiling at 76°C, was stored at −20°C until used. Ethyl acrylate was washed free of inhibitor with 5% sodium hydroxide–20% sodium chloride solution, dried over calcium sulfate, and stored at −20°C until used. The preparation of *n*-octadecyl acrylate has been described.[18]

Polymerization Procedure

The terpolymers were all polymerized in sealed bottles under nitrogen in benzene (4 moles/mole total monomer) at 60°C, generally for 72 hr, using 0.20 mole-% of bisazoisobutyronitrile as initiator. A few were run for 48 and 96 hr with no appreciable effect on the conversions. Terpolymer systems containing up to 50 mole-% acrylonitrile formed clear viscous solutions; from those richer in acrylonitrile, polymer precipitated. All of the polymers were isolated in methanol (5 ml/ml polymer solution), extracted free of monomer with refluxing methanol (5 ml/g polymer), and dried as fluffy solids or from thin films under vacuum at 50°C. The ethyl acrylate copolymer containing 30 mole-% acrylonitrile was extracted with petroleum ether. Yields of all terpolymers were between 70% and 85%. Elemental analyses for carbon and nitrogen were used to determine terpolymer compositions. These will be discussed in a later section.

Osmometric molecular weights were determined by reported procedures[5] except that toluene was the only solvent used and single determinations were done on each sample

Mechanical Properties

The procedures of references 3 and 5 were followed.

Calorimetric Procedure

The operation of the differential scanning calorimeter has been described for the determination of side-chain crystallinity[16,18] and glass transition temperatures.[17] All calculations and mathematical correlations were made with an IBM 1130 computer.

RESULTS AND DISCUSSION

General Features

The feed, polymer compositions, and degrees of polymerization are listed in Table I for all of the data collected. Sets of copolymers of acrylonitrile and ethyl acrylate were modified by successive gradual replacement of ethyl acrylate by *n*-octadecyl acrylate in each set. The postulated effect on the glass transition temperature for the copolymer and terpolymers of this investigation is shown schematically in Figure 1. The successive drop in T_g for the base copolymer of each set is on the ordinate, between the top and bottom lines; the further decline is produced by the weight fraction of *n*-octadecyl acrylate, w_{OA}, incrementally replacing ethyl acrylate in each recipe. These calculations assume additivity in the depression of T_g by both ethyl and *n*-octadecyl acrylates. Additivity was found in this work for the ethyl acrylate–acrylonitrile copolymers. It was abundantly confirmed for many copolymers containing *n*-octadecyl acrylate,[17] including copolymers of *n*-octadecyl acrylate and acrylonitrile (top line in Fig. 1.) and *n*-octadecyl acrylate and ethyl acrylate[17] (bottom line in Fig. 1.). The terpolymers of this study lie between these extremes. The vertical

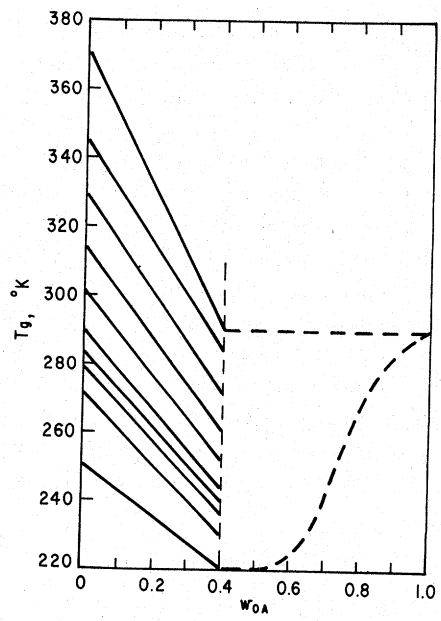

Fig. 1. Postulated effect on glass transition temperature. Solid lines are calculated values of T_g vs. weight fraction of *n*-octadecyl acrylate. Top line is for copolymers of *n*-octadecyl acrylate and acrylonitrile; bottom line is for copolymers of *n*-octadecyl acrylate and ethyl acrylate. The ordinate therefore represents T_g for copolymers of ethyl acrylate and acrylonitrile. Other lines are for terpolymers and follow the order of Tables I and II. Within the heavy dashed region, T_g is raised by side-chain crystallinity.

TABLE I

Compositions and Degrees of Polymerization of the Terpolymers[a]

Experiment no.	AN mole fraction in feed	Terpolymer composition[b]							
		Mole fraction			Wt. fraction				
		OA	EA	AN	OA	w_b[c]	n_b[d]	MW_b[e]	$\overline{DP}_n$
1	0.90	0	0.084	0.916	0	0.148	2.0	100.1	
2		0.032	0.032	0.936	0.164	0.214	14.2	271.5	
3		0.065	0	0.933	0.307	0.307	18.0	324.5	
4	0.80	0	0.144	0.856	0	0.241	2.0	100.1	
5		0.027	0.082	0.891	0.137	0.264	10.3	216.6	
6		0.064	0.064	0.873	0.282	0.396	14.2	271.5	
7		0.105	0.035	0.860	0.409	0.451	16.5	303.6	
8	0.70	0	0.239	0.761	0	0.372	2.0	100.1	
9		0.037	0.187	0.776	0.169	0.428	8.3	188.5	
10		0.081	0.162	0.758	0.317	0.513	11.9	238.9	
11	0.60	0	0.338	0.662	0	0.491	2.0	100.1	
12		0.047	0.273	0.681	0.193	0.541	7.7	180.4	436.5
13		0.093	0.265	0.642	0.334	0.625	10.5	251.0	375.2
14		0.128	0.213	0.659	0.424	0.642	12.6	148.2	364.3
15	0.50	0	0.473	0.527	0	0.629	2.0	100.1	
16		0.047	0.420	0.534	0.177	0.669	6.2	159.6	510.2
17		0.101	0.405	0.493	0.330	0.738	9.2	200.6	514.8
18		0.143	0.334	0.522	0.432	0.743	11.3	230.7	478.1
19		0.194	0.290	0.516	0.527	0.770	13.0	251.6	498.7
20		0.294	0.196	0.510	0.672	0.810	15.3	286.3	451.9
21		0.176	0.441	0.383	0.471	0.833	11.0	226.9	478.5
22	0.45	0	0.549	0.451	0	0.697	2.0	100.1	
23		0.049	0.485	0.466	0.177	0.722	5.9	155.1	554.5
24		0.097	0.435	0.468	0.314	0.751	8.7	194.0	495.0
25		0.144	0.385	0.470	0.425	0.774	10.8	207.2	490.1
26		0.194	0.341	0.465	0.517	0.798	12.4	245.7	396.8
27	0.40	0	0.603	0.397	0	0.741	2.0	100.1	0
28		0.049	0.536	0.415	0.173	0.759	5.6	151.1	614.4
29		0.100	0.501	0.398	0.313	0.797	8.3	188.4	581.4
30		0.146	0.439	0.415	0.419	0.806	10.3	216.6	477.8
31		0.200	0.401	0.399	0.515	0.832	11.9	238.8	511.8
32		0.300	0.300	0.401	0.655	0.857	14.2	271.6	523.2
33	0.30	0	0.694	0.306	0	0.811	2.0	100.1	479.5
34		0.099	0.594	0.307	0.298	0.849	7.6	178.9	544.6
35		0.121	0.560	0.319	0.351	0.850	8.6	192.7	474.3
36		0.147	0.540	0.313	0.403	0.860	9.5	205.2	449.4
37		0.170	0.510	0.321	0.447	0.862	10.3	216.6	499.3
38		0.197	0.492	0.312	0.493	0.872	11.0	226.9	551.6
39		0.243	0.439	0.318	0.565	0.879	12.3	244.2	482.2
40		0.298	0.399	0.302	0.634	0.895	13.3	259.0	466.5

[a] AN, Acrylonitrile; OA, *n*-octadecyl acrylate; EA, ethyl acrylate.

[b] Acrylonitrile computed from per cent nitrogen; *n*-octadecyl and ethyl acrylate calculated from per cent carbon on the assumption of equal reactivity with acrylonitrile.

[c] Composite plasticizer weight fraction, defined as $w_b = w_{OA} + w_{EA}$, where w_i is weight fraction.

[d] Composite weight-average plasticizer side-chain length, defined as $n_b = (w_{EA}/w_b)\,2.0 + (w_{OA}/w_b)\,18.0$.

[e] Composite weight-average plasticizer-unit molecular length, defined as $MW_b = (w_{EA}/w_b)MW_{EA} + (w_{OA}/w_b)MW_{OA}$.

dashed line marks the composition region where the onset of side-chain crystallinity should occur and begin to influence the glass transition temperature.[17] The sigmoidally bounded heavy dashed-line region indicates, schematically, the expected rise in T_g beyond this point. The top heavy dashed line represents, approximately, the observed T_g of crystalline *n*-octadecyl acrylate[17] and copolymers of this monomer with acrylonitrile.[17] This line is close to room temperature. Consequently, mechanical properties obtained on samples whose glass transitions lie above the line are for glassy terpolymers; those below the line are for terpolymers in the transition region.

Before proceeding further, a brief discussion of the feed composition and terpolymer compositions found by analysis seems appropriate. Per cent conversions were between 70% and 85% for these terpolymers. Copolymerization parameters for *n*-octadecyl acrylate[19] and ethyl acrylate[12b] are similar. The derived reactivity ratios for copolymerization with acrylonitrile predict the instant copolymer to be richer in acrylonitrile, with some drift in composition with conversion. The acrylonitrile content of the copolymers and terpolymers (Table I) was greater than in the feed as required. After correction for the nitrile content, obtained from the determination of nitrogen, the ethyl and *n*-octadecyl acrylate compositions were calculated from elemental analysis for carbon on the assumption that each acrylate has equal reactivity toward acrylonitrile. The assumption of equal reactivity of homologs in copolymerization has been abundantly confirmed.[20,21] From calculations based on the drift in composition with conversion,[22] but using the explicit conversion method of Kruse,[23] the calculated and found nitrile composition at each experimental conversion for the first five ethyl acrylate–acrylonitrile copolymers in Table I were found to be identical within experimental error. For the remainder, the calculated nitrile contents were higher higher by about 10%. It is of interest that this deviation occurs at compositions yielding soluble terpolymers. Anomalous reactivity ratios have been reported for precipitation polymerizations involving acrylonitrile[24] compared to solution polymerization. Consequently, the compositions of the soluble terpolymers might change somewhat as the systems become no longer dependent on adventitious comonomer concentrations at heterophase loci of polymerization. On the other hand, the known errors in nitrogen analysis at low nitrile contents, influencing reactivity ratios and therefore compositional drift with conversion, might also produce deviations of this magnitude. The degrees of polymerization (Table I) and the data correlations were based on the found composition of the terpolymer.

The mechanical properties, heats of fusion, and transition temperatures are listed in Table II for all of the copolymers and terpolymers. The glass transition decreased with increases in octadecyl acrylate, as would be expected. Details will be discussed in the next section. A reversed correspondence was found in this work between the Clash-Berg flex temperatures, T_f, and the glass transition temperature, T_g. Here, T_f values are much

higher than T_g values. This contrasts with data on methyl methacrylate copolymers plasticized by the higher n-alkyl acrylates,[13] where glass transition temperatures were slightly higher than flex temperatures. It was observed that the DSC scans were very broad for experiments 1 through 14 in Table II, suggesting a distribution of T_g values brought about by sample heterogeneity. Because the lower-onset temperature was taken as the T_g,[17] the high T_f values might reflect a higher average of the distribution. It is pertinent that for terpolymers having lower acrylonitrile contents (last four systems in Table II), where homogeneous terpolymerizations were observed, the glass transition region was relatively short, and T_f and T_g more nearly correspond. As in the previous study,[13] T_f seemed less sensitive to side-chain crystallinity than T_g.

Within each set in Table II, there was a marked decline in the tensile and flexural strengths and moduli. This trend applied even in the samples (selected from the first four sets in Table II) where the glass transition temperature was above or near room temperature. This decline in mechanical properties in the pretransition region was noticed before in copolymers of the n-alkyl acrylates and N-n-alkylacrylamides with methyl methacrylate[13] and in polystyrene plasticized with several external plasticizers.[25] A disordering of the glassy matrix by free volume produced around chain ends was postulated to explain the observed behavior. This will be discussed further in a later section. When the glass temperature was lowered considerably below room temperature (remaining four sets, Table II), there occurred the expected rapid decrease in moduli and strengths indicative of soft, plasticized compositions. At a critical weight fraction of n-octadecyl acrylate of about 0.4, the moduli and strengths rose somewhat, reflecting the restraints imposed by developing side-chain crystallinity.[13,16–18] The presence of crystallinity is indicated by the heats of fusion given in the table. These data again parallel the behavior found for methyl methacrylate copolymers plasticized with the same fatty comonomers.[13] Thus, to a first approximation at least, there were no great differences in behavior between the relatively nonpolar methacrylate copolymers and those discussed here where polar restraints from the nitrile groups could be expected to influence results. In similar fashion, the per cent elongations denoted brittle failure in the glassy terpolymers, but deformation instabilities[26] and flow when the transition region corresponded to or declined below room temperature. This behavior, too, had been observed for the methyl methacrylate copolymers and terpolymers.[13]

Glass Transition–Composition Correlations

The postulated decline in T_g with composition was discussed above and was described in Figure 1. Found values are given in Figure 2. As can be seen, the correspondence was fairly good, and deviations, caused by side-chain crystallinity,[17] occurred near a weight fraction of 0.4 n-octadecyl acrylate. The deviation in the same vicinity for curve 1 in the figure is not understood, because crystallinity was absent. It may be that electrostatic

TABLE II

Mechanical Properties, Heats of Fusion, and Transition Temperatures Found for Terpolymers

Experiment no.[a]	AN mole fraction in feed	Glass and flex temperatures, °C		Flexural properties		Tensile properties			ΔH_f, cal/g
		T_g	T_f	Strength, psi	Modulus, psi × 10^{-5}	Strength, psi	Modulus,[b] psi × 10^{-5}	Elongation, %	
1	0.90	70.9	84.0	5450	2.20	3129	2.02	2	0
2		34.9	66.0	3108	1.39	1137	1.93	1	0
3		28.9	48.0	1630	0.721	219	0.659	1	0
4	0.80	54.9	71.0	7153	3.25	4286	2.18	2	0
5		22.9	58.0	4455	2.12	3300	1.62	2	0
6		36.9	45.0	3114	1.50	1619	1.37	2	0
7		−3.1	34.0	2064	0.983	629	0.810	2	0.87
8	0.70	39.9	54.5	5810	2.63	8550	2.37	4.5	0
9		12.9	32.0	2600	1.21	3940	1.02	6.9	0
10		−7.1	38.0	2680	1.25	2910	1.03	3.0	0
11	0.60	27.9	40.0	4245	1.98	5897	2.06	35.0	0
12		3.9	16.0	782.7	0.365	3210	0.682	65.0	0
13		−15.1	24.0	1206	0.575	2836	0.665	70.0	0
14		−19.1	60.0	1591	0.692	3825	0.599	15.0	0.64
15	0.50	16.9	20.0	1020	0.470	2260	0.739	67.4	0
16		−3.1	9.0	104.0	0.048	1790	0.018	294	0
17		−35.1	−3.5	57.4	0.028	1530	0.013	365	0
18		−16.5	−5.0	634.0	0.032	1720	0.058	22.5	0.56
19		−21.1	−3.0	1051	0.519	2230	0.479	13.2	2.78
20		−2.8	−20.0	1040	0.540	1110	0.403	2.9	7.28
21		12.9	−27.0	1015	0.526	323	0.300	1.3	10.7

22	0.45	12.5	25.0	457.0	0.209	1690	0.130	121	0
23		−8.1	6.0	15.1	0.007	1450	0.008	368	0
24		−28.1	−12.0	—	—	1420	0.005	458	0
25		−35.1	−8.0	115.0	0.057	1050	0.011	266	0.63
26		−38.1	−4.0	415.0	0.206	1690	0.405	108	3.56
27	0.40	6.9	13.5	—	—	1290	0.010	306	0
28		−13.1	−2.5	—	—	723	0.003	448	0
29		1.9	−13.0	—	—	515	0.001	587	0
30		−40.1	−18.0	38.0	0.018	592	0.006	412	1.03
31		−28.1	−17.0	179.0	0.086	924	0.009	113	4.36
32		6.9	−21.0	773.0	0.371	58	0.008	10	8.84
33	0.30	−3.1	−5.0	—	—	365	0.001	578	0
34		−33.1	−25.0	—	—	96	0.0004	1260	1.09
35		−6.1	−79.0	—	—	81	0.0005	829	2.52
36		4.9	−46.0	—	—	316	0.001	922	5.44
37		7.9	−38.0	—	—	215	0.003	513	5.61
38		−5.6	−33.0	64.7	0.031	451	0.006	224	6.69
39		4.9	−36.0	195.0	0.101	632	0.158	85	9.16
40		10.9	−52.0	526.0	0.256	1330	0.227	6.3	11.49

[a] Experiments correspond to those in Table I.

[b] Secant moduli, except when elongations exceeded 100%, when they are 100% moduli.

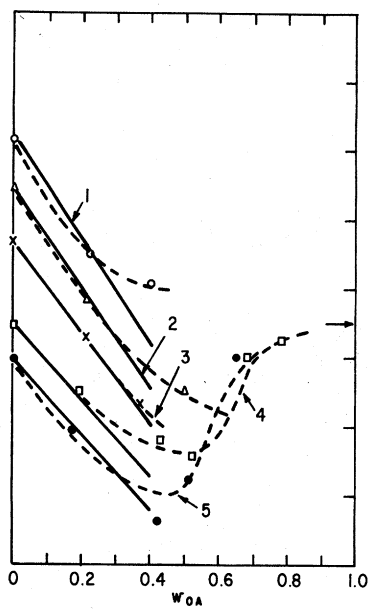

Fig. 2. Found values of effect of composition on glass transition temperature. Selection of experimental data (dashed lines) with repeated calculated data (solid lines). Mole fraction acrylonitrile in feed: (1) 0.90; (2) 0.80; (3) 0.70; (4) 0.50; (5) 0.40.

interactions, leading to stiff acrylonitrile chains, and initially reduced by small amounts of the 18-carbon acrylate became intensified because of greater aggregation of the side chains at higher octadecyl acrylate contents.[6c] This would only be expected in terpolymers especially rich in acrylonitrile. The effect of each methylene in the side chain on the glass transition will now be discussed.

It was established in the previous publication of this series[13] that the decline in T_g with weight fraction of long side-chain acrylate or acrylamide in methyl methacrylate copolymers was directly proportional to the free volume fraction introduced by each added methylene group present in the side chain of the plasticizing co-unit. The relations established for this system should be quite general and apply equally well to the terpolymers of this investigation. Thus, the contribution to lowering the apparent molecular weight of the total plasticized system by chain-end plasticization[27] will depend on the number of methylene groups present in side chains[13] as well as on the number of side chains creating chain ends. The effect on lowering the glass transition of polymers by accumulated chain-end imperfections was first proposed by Fox and Flory[28] and is stated as

$$T_g = T_{g\infty} - c/\overline{M}_n \tag{1}$$

where $T_{g\infty}$ is the glass transition temperature of a hypothetical polymer of infinite molecular weight having essentially no chain ends, $\overline{M}_n$ is the number-average molecular weight, and c is a constant characteristic of the

system. Equation (1) was rederived[13] to apply to copolymers having units contributing long linear side chains and became

$$T_g = T_{ga} - c_p(w_b/MW_b) \tag{2}$$

where T_{ga} is the T_g for the high molecular weight amorphous homopolymer being plasticized, w_b is the weight fraction of comonomer having a long side chain, MW_b is the molecular weight of its unit, and c_p is the proportionality constant. Throughout this paper, the subscript a will refer to acrylonitrile, while the subscript b will refer to the sum of ethyl and n-octadecyl acrylate present. Weight fractions of either ethyl or n-octadecyl acrylate are in turn designated w_{EA} and w_{OA}, respectively. It was further shown[13] that c_p for a homologous series was proportional to side-chain length through

$$c_p = c_{p0} + C(n) \tag{3}$$

where n was the number of methylene groups in the side chains and C was a constant expressing the contribution of each added methylene group to generating free volume at T_g. In this equation, c_{p0} becomes an empirical stiffness constant characteristic of the internal plasticizer. By use of a modified equation of Bueche,[29]

$$c_p = \rho N \phi / \alpha \tag{4}$$

where ρ is the density of the homopolymer, N is Avagodro's number, $\alpha = \alpha_l - \alpha_g$ is the expansion coefficient difference between the liquid and glassy state, and ϕ is the free volume in cc per mole of chain ends, it was demonstrated[13] that in systems internally plasticized by monomers having linear side chains, the free volume contributed by each methylene group at T_g could be estimated. Thus, by differentiating eq. (3) after substituting from eq. (4),

$$\phi_n = C/[\rho N(1/\alpha)] \tag{5}$$

The free volume ϕ_n per side-chain methylene for both the n-alkyl acrylates and N-n-alkylacrylamides were calculated[13] by eq. (5) to be 1.6 and 1.5 Å^3, respectively. A similar estimation can be made using the data of this work on terpolymers.

Correlation of the T_g and the weight fraction of ethyl acrylate, w_{EA}, for the base copolymers was made in accordance with

$$T_g = T_{ga} - k w_{EA}, \tag{6}$$

and the parameters are given in Table III. With c_p defined as $k\ MW_b$, from eq. (2), values of c_p were computed for the ethyl, n-butyl, 2-ethylhexyl, and n-octadecyl acrylates copolymerized with acrylonitrile. For the n-octadecyl acrylate copolymers, k came from Table III of reference 17. The glass transition temperatures, determined experimentally for poly(n-butyl acrylate) and poly(2-ethylhexyl acrylate) and for polyacrylonitrile, were from Table I of the same reference. These were used to calculate c_p for the acrylate–nitrile copolymers having n equal to 4 and 8, respectively. For c_p the quantity $(T_{ga} - T_{gi})MW_i$, was used where the subscript i refers

TABLE III

Curve-Fitting Parameters for Pretransition-State Mechanical Properties[a] and for Relation of Glass Transition Temperatures to Composition for Ethyl Acrylate and Acrylonitrile Copolymers

Parameter[b]	A_0	B[c]
Flexural modulus, psi	$(2.23 \pm 0.17) \times 10^5$	$(3.75 \pm 0.65) \times 10^5$
Flexural strength, psi	$(5.01 \pm 0.36) \times 10^3$	$(8.70 \pm 1.39) \times 10^3$
Tensile modulus, psi	$(2.18 \pm 0.10) \times 10^5$	$(3.77 \pm 0.41) \times 10^5$
Tensile strength, psi	$(5.06 \pm 0.47) \times 10^3$	$(9.20 \pm 1.90) \times 10^3$
Copolymer EA + AN T_{ga} and k of eq. (6)	359.0°K ± 2.40	109.8°K ± 4.03

[a] Experiments 1 through 14 of Table II. Excluded were: flexural moduli and strengths, exps. 4 and 12; tensile moduli, exps. 9 and 12; tensile strengths, exps. 1–3, 8, and 14.

[b] Designations as in eqs. (7)–(11): flexural modulus, E_f; flexural strength, FS; tensile moduli, E_t; tensile strength, TS.

[c] Designations as in eqs. (9) and (11): flexural modulus and strength, α, β; tensile modulus and strength, γ, δ.

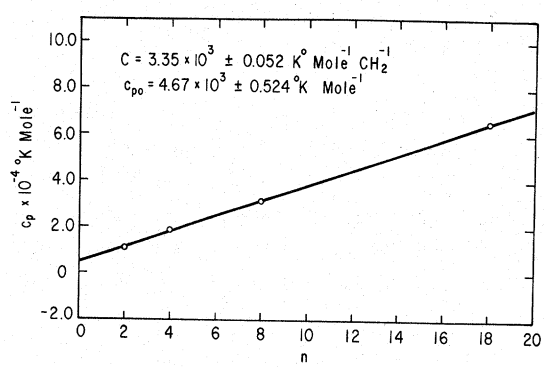

Fig. 3. Plots of c_p vs. the number n of methylene groups in side chain of n-alkyl acrylate homopolymers.

to either butyl or 2-ethylhexyl acrylate. The relation between c_p and the side-chain length n is given in Figure 3. The parameters C and c_{p0}, were similar to those for the methyl methacrylate systems[13] because of the similarity of T_g for the two stiff homopolymers. Again, the free volume per methylene group in the side chains was 1.6 Å^3, using the same quantities for the calculation as were used in reference 13. It remains to show in a more quantitative manner the relation between the glass transition temperatures of the terpolymers and their mechanical properties. Before proceeding, however, the correlation between the mechanical properties and terpolymer composition will be discussed briefly.

Mechanical Property–Composition Correlation

The mechanical property data for the first four sets in Table II were obtained at 23°C, and consequently below or near the transition temperature.

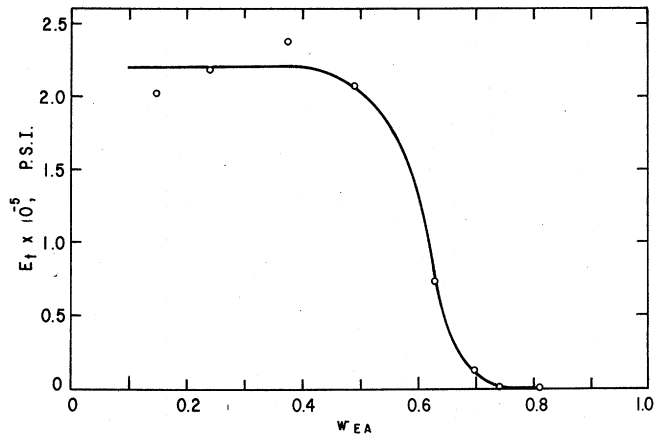

Fig. 4. Tensile moduli vs. weight fraction of ethyl acrylate in copolymers of ethyl acrylate and acrylonitrile.

Plots of the combined data for all four sets against the weight fraction of *n*-octadecyl acrylate fell near a common line for each mechanical property. The data were fitted by computer using the relation

$$A = A_0 + Bw_{OA} + B'w_{OA}^{2} + \ldots \quad (7)$$

where A is designated the mechanical property, A_0 is the property for polyacrylonitrile, and B and B' are the coefficients corresponding to the degree in w_{OA}. The parameters, significant to the first degree only, are listed in Table III. Correlations were made against the weight fraction of only *n*-octadecyl acrylate because ethyl acrylate alone had little effect on reducing the moduli or ultimate strengths. This can be seen in Figure 4, which shows the tensile moduli, typical of all of the mechanical data, plotted against the weight fraction of ethyl acrylate. The moduli did not drop until the transition region corresponded to room temperature or below. Clearly, only the long *n*-alkyl ester reduced moduli in the pretransition region. On the other hand, in accordance with eq. (3), both esters contribute to a decline in T_g. These observations suggest that the cooperative motion of the sequences of chain segments responsible for the glass transition phenomena[30] are sensitive to subgroups of any length. However, side chains of a critical length are necessary to reduce mechanical properties in the glassy matrix. This critical length seems to occur at about a methylene chain length of four, because *n*-butyl acrylate and N-*n*-butylacrylamide reduced the mechanical properties of methyl methacrylate[17] to some extent. It may be that subgroup motions of the "crankshaft" type[31] are required to initiate the larger strains. In a different view, phase separation of side chains could occur beyond a critical length, thus introducing volume elements that act as stress concentrators. In support of the latter idea, all of the glassy terpolymers exhibited brittle failure.[26]

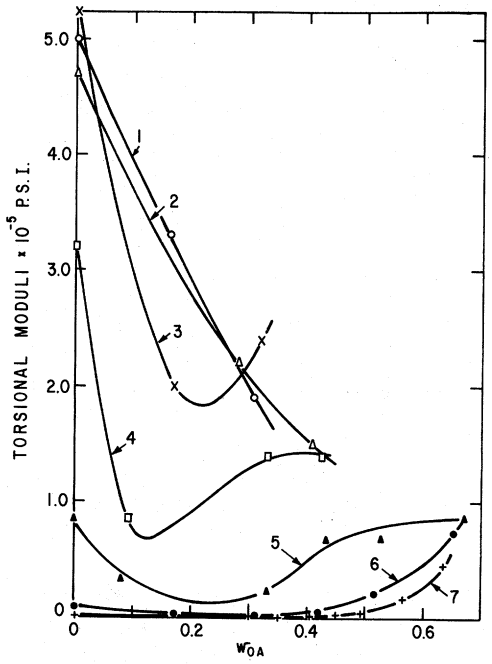

Fig. 5. Torsional moduli at 23°C vs. weight fraction of *n*-octadecyl acrylate in selected terpolymer systems. Mole fraction of acrylonitrile in feed: (1) 0.90; (2) 0.80; (3) 0.70; (4) 0.60; (5) 0.50; (6) 0.40; (7) 0.30.

When the temperature of testing corresponded to the transition temperature, moduli and strengths declined precipitously, and soft plasticized compositions were obtained. This is shown clearly in Figure 5, where torsional moduli, taken from the Clash-Berg curves at room temperature, are plotted against the weight fraction of *n*-octadecyl acrylate. Curves 4 to 7 were measured through and below the transition region and illustrate the magnitude of plasticization achieved. The rise in moduli at high weight fraction of ester in curves 3 and 4 is not understood. Only experiment 14 (Tables I and II) exhibited measurable crystallinity. Again, aggregation of side chains leaving naked dipoles which then associate might be responsible for the behavior. The increasing moduli of curves 5, 6, and 7 at high w_{OA} can be attributed to restraints imposed by side-chain crystallinity.[16,17] The moduli increase was accompanied by a marked increase in resilience and by a decrease in dampening compared to noncrystalline specimens. Again, the moduli of the ethyl acrylate–acrylonitrile copolymers for curves 1–4 (at the ordinate) showed little decline as acrylate content increased.

Tensile strengths and elongations for experiments 16–18, 23–25, and 28 were similar to the vulcanizates of copolymers of *n*-butyl acrylate containing minor amounts (12.5 mole-%) of acrylonitrile. The latter systems were studied many years ago.[14] Of course, the terpolymers of this work are thermoplastic and require no reinforcing filler. This suggests that the incorporation of large amounts of acrylonitrile in these terpolymers, al-

lowed by the better plasticization efficiency of n-octadecyl acrylate, permitted greater network reinforcement through intermolecular dipole interactions. Dipole interactions, proposed[10] to account for the 140°C transition in polyacrylonitrile, could act as a network in the polymer matrix. Tensile strengths would thereby be substantially increased, without recourse to vulcanization.

Correlation of the Glass Transition Temperature with the Mechanical Properties of the Glassy Region

Attempts to correlate the glass transition and the mechanical data even in the glassy region lead to a complication. It was noted above that both ethyl and n-octadecyl acrylate contribute to the glass transition temperature, while only the 18-carbon ester affects mechanical properties. To be successful a correlation equation must calculate T_g while compensating for the reduced effect of ethyl acrylate on the mechanical properties. An empirical equation was developed for calculating tensile moduli E_t for the glassy terpolymers only. The equation is

$$E_t = [B_0 - \omega(T_{ga} - kw_{\mathrm{EA}})] + K(T_{g\mathrm{AN}} - [(c_{p0} + C(n_b))/MW_b]w_b) \qquad (8)$$

The portion of eq. (8) at the right, within the parentheses, calculates a T_g for any value of n_b, MW_b, and w_b. Values for the last three quantities applied to the data of this work are listed in Table I. The b subscript denotes weighted quantities of ethyl acrylate and n-octadecyl acrylate as defined in Table I. The constants c_{p0} and C are given in Figure 3, and the glass transition temperature of polyacrylonitrile, $T_{g\mathrm{AN}}$ was shown experimentally[17] to be 365.1°K. The calculated T_g is proportional to tensile moduli through the constant K and a quantity to the left of K, within the square brackets, based on the T_g of the base copolymers, modified by adjustable parameters B_0 and ω. Numerical values of the parameters were found by trial to be: K, 2650 psi °K; B_0, 280,000 psi; and ω, 2850 psi °K. The values of T_{ga} and k are from Table III. The other mechanical properties were assumed to be proportional to E_t, as expressed in eqs. (9) through (11):

$$TS = E_t/(\gamma/\delta) \qquad (9)$$

$$E_f = 1.067E_t \qquad (10)$$

$$FS = E_f/(\alpha/\beta) \qquad (11)$$

where TS is tensile strength, E_f is flexural modulus, and FS the flexural strength. The other quantities in the equations are defined and their numerical values given in Table III. Mechanical properties calculated using eqs. (8) through (11) are compared in Table IV with values calculated as smoothed data, using the constants A_0 and B of Table III. The satisfactory agreement suggests that eq. (8) is in fact sufficiently sensitive to the free volume contributed by each methylene group to the reduction of the glass temperature, while adjusting the proportionality to properly yield the decrease in mechanical properties conferred by the long side-chain ester

TABLE IV
Comparison of Mechanical Properties Calculated Using Equations (8)–(11) with Smoothed Found Values[a]

Exp. no.	w_{OA}	$E_t \times 10^{-5}$, psi		TS, psi		$E_f \times 10^{-5}$, psi		FS, psi	
		Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
Acrylonitrile Feed, mole fraction 0.90									
1	0	2.27	2.18	5539	5060	2.32	2.23	5212	5010
2	0.164	1.62	1.56	3956	3553	1.65	1.62	3707	3585
3	0.307	1.09	1.02	2655	2237	1.11	1.08	2494	2341
Acrylonitrile Feed, mole fraction 0.80									
4	0	2.28	2.18	5561	5060	2.33	2.23	5234	5010
5	0.137	1.74	1.66	4246	3799	1.77	1.72	3977	3818
6	0.282	1.12	1.12	2738	2467	1.14	1.17	2561	2557
7	0.409	0.645	0.638	1574	1298	0.658	0.697	1478	1453
Acrylonitrile Feed, mole fraction 0.70									
8	0	2.29	2.18	5592	5060	2.34	2.23	5257	5010
9	0.169	1.46	1.54	3556	3509	1.49	1.59	3348	3544
10	0.317	0.878	0.983	2142	2140	0.896	1.04	2013	2249
Acrylonitrile Feed, mole fraction 0.60									
11	0	2.30	2.18	5621	5060	2.35	2.23	5279	5010
12	0.193	1.35	1.45	3304	3281	1.38	1.50	3100	3327
13	0.334	1.14	0.922	2790	1991	1.16	0.979	2606	2108
14	0.424	0.577	0.583	1407	1162	0.589	0.641	1323	1324

[a] Smoothed data calculated using eq. (7).

only. Thus, the simple dependence of T_g and the mechanical strength and moduli on the volume effects of side chains existing as aggregates in the glassy terpolymers can be adequately described by the equation. A similar result was found for methyl methacrylate copolymers internally plasticized by the *n*-alkyl acrylates and N-*n*-alkylacrylamides.[13]

SUMMARY

In this work, the glass transition temperatures of base copolymers of acrylonitrile and ethyl acrylate, of all compositions, were further modified through terpolymerization with *n*-octadecyl acrylate. The ethyl acrylate was incrementally replaced by *n*-octadecyl acrylate in the termonomer feed. Thus, vitreous transitions could be reduced to a wide range of low temperatures because *n*-octadecyl acrylate efficiently reduced the T_g of the base copolymers as ethyl acrylate successively replaced nitrile. Soft, plasticized compositions resulted which still contained sufficient polar nitrile networks to confer useful properties. The decline in the glass transition was shown to be dependent on the free volume conferred by each methylene group of each acrylate unit, while only the 18-carbon side chains contributed to the decline in tensile and flexural moduli and strengths of the glassy composi-

tions. An equation was developed which correlated empirically the glass transitions and the mechanical properties with the weight fractions of the acrylate esters.

The authors thank Dr. C. L. Ogg, Miss Oksana Panasiuk, Mrs. Marta T. Lukasewycz, and Mrs. Annette S. Kravitz for the elemental analysis of the copolymers and terpolymers. They are especially thankful to Mr. Bohdan Artymyshyn for the number-average molecular weights and to Mrs. Ruth D. Zabarsky for the operation of the computer.

Reference to brand or firm name does not constitute endorsement by the U.S. Department of Agriculture over others of a similar nature not mentioned.

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Received May 25, 1972