first interesting point is that there is no steric overlap of L and D side chains in $(\mathrm{LDLL})_n$; on the contrary, the nonbonded side-chain–side-chain interactions in $(\mathrm{LDLL})_n$ are more favorable than in $(\mathrm{L})_{4n}$ because of the proximity of the methyl group of a D residue to the methyl group of the third next L residue. In fact, calculations show that there is no steric hindrance even in the regular-sequence alternating D,L copolymer.[4]

Regarding the question as to which helical sense, the right- or the left-handed one, has the lowest energy, Ooi *et al.*[15] showed that the polypeptide backbone of an α helix formed from L residues does not show much preference for helix sense, *i.e.*, α_{RH} or α_{LH}. Because of the fact that, in general, L side chains are somewhat nearer to the backbone in the right-handed conformation than in the left-handed one, the resulting favorable nonbonded side-chain–backbone interactions (see Table IV) bring about a preference for the right-handed α-helical conformation for L_{4n} and *to a lesser degree* also for $(\mathrm{LDLL})_n$. The uniform side-chain–backbone conformation for L_{4n} is disturbed in $(\mathrm{LDLL})_n$ because D side chains are not as near to the right-handed α-helical backbone as L side chains are, and this unfavorable effect is greater than the energy gain from side-chain–side-chain interactions. Therefore, the energy of the right-handed α helix is slightly less favorable for $(\mathrm{LDLL})_n$ than for L_{4n} (see Figure 10). On the other hand, the left-handed α helix has a lower energy for $(\mathrm{LDLL})_n$ than for L_{4n} (see Figure 10) because of both more favorable (compared to all-L) side-chain–side-chain and side-chain–backbone interactions.

In conclusion, comparing the energies of the two helical conformations of $(\mathrm{LDLL})_n$, we find that the right-handed α helix has a lower energy than the left-handed α helix; however, the difference in energy is only about half of the difference found for L_{4n} (see Figure 10). Because of limitations in the accuracy of the calculations, we do not wish to place too much reliance on the absolute values of Δ(RH–LH). Instead, we would conclude that, whereas Δ(RH–LH) indicates that the right-handed α-helical form of poly(L-alanine) is more stable than the left-hand one, there is less preference for the right-handed one in poly(LDLL-alanine). Therefore, the latter polymer would be more likely to consist of a mixture of right- and left-handed helices, with a predominance of the right-handed form, as also concluded from the experimental data.

F. Concluding Remarks. The nature of this mixture of helices and random coils can be deduced from the cooperative nature of the helix-coil equilibrium in poly(α-amino acids). For an infinitely long polymer at the midpoint of the transition ($\theta = 0.5$), the average length of a helical sequence is $\sigma^{-1/2}$, where σ is the Zimm–Bragg nucleation parameter.[28] For most poly(α-amino acids), this length is about 50 residues.[29] Thus, we may conclude that, for the short oligopeptides considered here, the transition is of the "all-or-none" type; *i.e.*, a given molecule is either a random coil or a right- or left-handed α helix.

---

(28) B. H. Zimm and J. K. Bragg, *J. Chem. Phys.*, 31, 526 (1959).

(29) N. Lotan, A. Berger, and E. Katchalski, *Annu. Rev. Biochem.*, 41, 869 (1972).

Sequence Distribution–Glass Transition Effects. III. α-Methylstyrene–Acrylonitrile Copolymers

N. W. Johnston

Union Carbide Corporation, Research and Development, Bound Brook, New Jersey 08865.

Received November 29, 1972

ABSTRACT: To predict the glass transition temperature (T_g) of many copolymers it is often necessary to take into consideration the sequence distribution of the polymer. Homopolymer T_g values usually hold for AA or BB dyads in the AB copolymers because the A or B units experience much the same interactions as in A or B homopolymers. The formation of AB dyads results in new interactions and in many cases changes the T_g contribution of the A unit. Therefore, to obtain accurate T_g predictions, it is sometimes necessary to assign AB dyads and other sequence distributions their own T_g values. This work reports the effect of sequence distribution on the T_g of α-methylstyrene–acrylonitrile copolymers. This system exhibits a strong T_g depression effect. This T_g depression effect, the use of alternating polymers in predicting T_g's and a group additive approach to polymer T_g's are discussed in this paper.

The glass transition temperatures of copolymers are usually predicted by additive relations such as the Fox equation[1]

$$(1/T_{\mathrm{gP}}) = (W_{\mathrm{A}}/T_{\mathrm{gA}}) + (W_{\mathrm{B}}/T_{\mathrm{gB}}) \qquad (1)$$

where T_{gp} is the T_{g} of a copolymer containing weight fraction W_{A} and W_{B} of the two monomer units A and B for which the homopolymers have glass transitions of T_{gA} and T_{gB}. The Fox and other similar relationships do not take into consideration the effect of adjacent dissimilar monomer units on steric and energetic relations in the copolymer backbone and assume that the freedom of rotation and free volume contributed to a copolymer by a given monomer will be the same as it contributes to the homopolymer. As pointed out in previous papers, the Fox type of relationship does not hold for all copolymers.[2,3]

---

(1) T. G. Fox, *Bull. Amer. Phys. Soc.*, 1, 123 (1956).

(2) N. W. Johnston, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, 10 (2), 609 (1969).

(3) N. W. Johnston, 8th Annual Plastics Institute of America Research Conference, Stevens Institute of Technology, Hoboken, N. J., Nov. 4, 1970; *J. Macromol. Sci.-Chem., Part A*, 7, 531 (1973).

To accurately predict the glass transition temperature of many copolymers it is necessary to take into consideration the sequence distribution of the polymer. Homopolymer T_g values usually hold for AA dyads in AB copolymers because the A units experience much the same interactions as in A homopolymers. The formation of AB dyads results in new interactions and in many cases changes the T_g contribution of the A unit. Therefore, to obtain more accurate T_g predictions, it is necessary to assign AB dyads and other sequence distributions their own T_g values.

The probabilities of having various linkages (P_{AB}, P_{AA}) may be calculated by computing the average run number (R)[4] for a given copolymer composition (A, B) and using eq 2 and 3

$$P_{AB} = R/2A \tag{2}$$

$$P_{AA} = 1.0 - P_{AB} \tag{3}$$

Using these probabilities, an equation may be written to predict the copolymer glass transitions which takes into consideration the copolymer sequence distribution and AA, BB, and AB glass transition temperatures.

$$\left[\frac{1}{T_{gP}}\right] = \left[\frac{W_A P_{AA}}{T_{gAA}} + \frac{W_A P_{AB} + W_B P_{BA}}{T_{gAB}} + \frac{W_B P_{BB}}{T_{gBB}}\right] \tag{4}$$

T_{gP} is the T_g of a copolymer containing weight fraction W_A and W_B of two monomer units A and B which have the probabilities P_{AA}, P_{AB}, P_{BA}, P_{BB} of having various linkages contributing T_g's of T_{gAA}, $T_{gAB} = T_{gBA}$, and T_{gBB} to the copolymer.

For the majority of cases we have found that using a T_{gAB} value for AB dyads is sufficient to predict sequence distribution–T_g effects in a series of copolymers. This assumes that one unlike neighbor will depress the copolymer T_g approximately as much as having a monomer unit between two unlike groups. Assigning a value of T_{gAB} to AB units, therefore, does not take into consideration such triads as BA*B, BA*A, or AA*B, where A* may contribute different T_g's to the copolymer. This assumption is not valid in all copolymer systems and we have found some copolymers that exhibit strong triad-T_g effects. For these cases or in the case of terpolymers, eq 4 was expanded to meet the appropriate situation.

T_{gAB} values have been determined by several techniques. One techique is to prepare an AB copolymer with a low B content. This copolymer would have most B units centered in ABA triads and a very low or negligible probability of BB. An experimental T_g (T_{gP}) would then be obtained and eq 4 used to solve for T_{gAB}. A second technique is to use the T_g's of a series of copolymers (eq 4) and a computerized multiple regression analysis program to solve for T_{gAB}.

A third technique for finding T_{gAB} values is the preparation of alternating copolymers. These polymers are prepared by complexing one monomer (A) with a complexing agent (X). The complexed monomer (XA) will form a dyad with the second monomer and then polymerize as a pair giving an alternating copolymer consisting entirely of A–B dyads. The T_g of an alternating copolymer would then be equal to T_{gAB} and could be used to predict the T_g's of random copolymers.

Experimental Section

Glass Transition Measurements. Glass transition temperatures of the polymers were measured using a Perkin-Elmer DSC-1B differential scanning calorimeter. An initial scan was made to produce a uniform thermal history in all polymers. The glass transition temperatures reported are the average of several additional scans at 10°/min and were reproducible to ±0.6°.

Table I
αMS–AN Copolymers

Sample No.	Polymerization Technique	Mol % αMS Feed	Mol % αMS Copolymer	$[\eta]$ dl g^{-1}
α-A-A	$ZnCl_2$	25.0	49.3	0.60
α-A-1	Bulk-free radical	10.0	36.2	0.56
α-A-2	Bulk-free radical	51.0	52.1	0.40
α-A-3	Emulsion-free radical	70.0	57.8	0.40
α-A-4	Emulsion-free radical	75.0	59.7	0.38
α-A-5	Emulsion-free radical	80.0	62.4	0.35

The literature often reports several different T_g's for the same homopolymer. The reason for this is frequently ascribed to the T_g's being obtained *via* different techniques. To add more validity to our DSC T_g measurements, we obtained T_g measurements on selected polymer samples using a DuPont Model 900 differential thermal analyzer and both the expansion and penetration mode of a DuPont Model 941 thermal mechanical analyzer. All three techniques provided T_g measurements within 1° of those obtained using the Perkin-Elmer DSC-1B.

Copolymer Preparation. A completely alternating copolymer of α-methylstyrene-acrylonitrile (αMS-AN) was prepared using a 0.1–1.0 *M* ratio of $ZnCl_2$ to AN and a 3:1 molar ratio of AN to αMS. This mixture was polymerized in bulk at 60° under N_2 atmosphere and yielded a polymer with an $[\eta]$ of 0.6 in 2-butanone. N and C analysis indicated the resulting polymer (α-A-A) to be 49 mol % αMS.

Five αMS-AN copolymers were prepared by free-radical polymerization at 60°. Copolymers α-A-1 and α-A-2 were prepared *via* bulk polymerization and α-A-3, α-A-4, and α-A-5 were prepared *via* emulsion polymerization to obtain $[\eta]$'s in the range of the other two copolymers. All conversions were kept below 2%. Table I lists monomer feeds, polymer compositions, and $[\eta]$'s for all six copolymers.

Theoretical Considerations

Group Additive T_g Approach. We have noted in our previous work that the glass transition temperature contribution of many monomers di-α-substituted with two large groups changes dramatically when these monomers are copolymerized with monomers not similarly substituted. A butyl methacrylate (BMA) monomer unit between two vinyl chloride (VCl) units in a BMA-VCl copolymer chain does not have a T_g contribution of 20°, the T_g of poly(butyl methacrylate).[3] The T_g of an isolated BMA[3] is −8.7 or ~32° higher than the reported T_g of −40° for poly(butyl acrylate).[5] A methyl methacrylate (MMA) unit between two VCl units has a T_g of 34.6[3] or ~29° higher than the reported T_g of 6° for poly(methyl acrylate).[6] For the two systems we have accumulated the most experimental evidence for (MMA-VCl and BMA-VCl), the T_g contribution of a methyl group substituted on an isolated alkyl methacrylate is ~30°. This value for the placement of a methyl group is quite reasonable considering the difference of 35° in the 200°K T_g of poly(*cis*-2-methyl-1,3-butadiene) and the 165°K T_g of poly(*cis*-1,3-butadiene).[6]

If the ~30° value for an isolated methyl group holds true, the T_g of an isolated αMS unit would not be the same as poly(α-methylstyrene) or 177°,[7] but should be ~130 or ~30° greater than the T_g of polystyrene. A com-

---

(4) H. J. Harwood and W. M. Ritchy, *J. Polym. Sci., Part B*, **2**, 601 (1964).

(5) F. P. Reading, J. A. Faucher, and R. D. Whitman, *J. Polym. Sci.*, **57**, 483 (1962).

(6) W. A. Lee and G. J. Knight in "Polymer Handbook," J. Brandrup and E. G. Immergut, Ed., Interscience Publisher, New York, N. Y., 1966.

(7) J. M. G. Cowie and P. M. Toporowski, *J. Macromol. Sci.-Phys., Part B*, **3**, 81 (1969).

Table II
αMS–AN Copolymer Glass Transition Temperatures

			T_g (°C)		
				Predicted	
Sample No.	Sequence Distribution	αMS (mol %)	Expt	Sequence Distribution[a]	Fox[b]
α-A-A	Alternating	49.3	122	122	151
α-A-1	Random	36.2	119	119	142
α-A-2	Random	52.1	125	126	153
α-A-3	Random	57.8	133	133	157
α-A-4	Random	59.7	135	135	158
α-A-5	Random	62.4	137	138	159

[a] Predicted using eq 4. [b] Predicted using eq 1.

pletely alternating αMS–AN copolymer would have only isolated αMS units and, therefore, would have an AN T_g contribution of ~105°[6] and an αMS T_g contribution of ~130°. The T_g of an alternating αMS–AN copolymer or the value of T_{gAB} may be predicted by using a weight–T_g relationship such as equation (1) and the fact that an αMS–AN dyad is ~31 wt % AN and ~69 wt % αMS. Based on these values an alternating αMS–AN copolymer was predicted to have a T_g of ~122°. After these predictions were made, an alternating αMS–AN copolymer was prepared. The following sections verify the predicted T_g of 122° for an αMS AN-dyad and illustrate the use of this value to predict T_g's for random αMS–AN copolymers.

Sequence Distributions. Sequence distributions were predicted using reactivity ratios of 0.17:0.088 determined for αMS–AN in this work and computer programs discussed in previous papers.[8] Although αMS–AN copolymers might be expected to exhibit penultimate type effects, we found the above terminal model reactivity ratios to fairly accurately predict experimental copolymer compositions. A penultimate effect on the sequence distribution of αMS–AN copolymers is, of course, possible. Our ability to measure the difference between terminal model and penultimate model sequence distribution effects on glass transition temperature at this time is doubtful.

Results and Discussion

The T_g's of the alternating and random αMS–AN copolymers were measured using DSC. The T_g of the alternating copolymer was predicted as previously discussed. The T_g's of the random copolymers were predicted using eq 4, a T_{gAB} value of 122°, a T_g of PAN of 105°[6] and T_g of PαMS of 177°.[7] Table II compares the experimental T_g's with values predicted using the sequence distribution–T_g relationship and those predicted using the Fox equation. Figure 1 shows a plot of weight per cent αMS in αMS–AN copolymers *vs.* the experimental, sequence distribution predicted, and Fox equation predicted T_g's for αMS–AN random copolymers. Glass transition plots using other T_g–copolymer relationships such as proposed by Wood[9] do not yield linear plots nor do they yield correct homopolymer T_g values for the αMS–AN system.

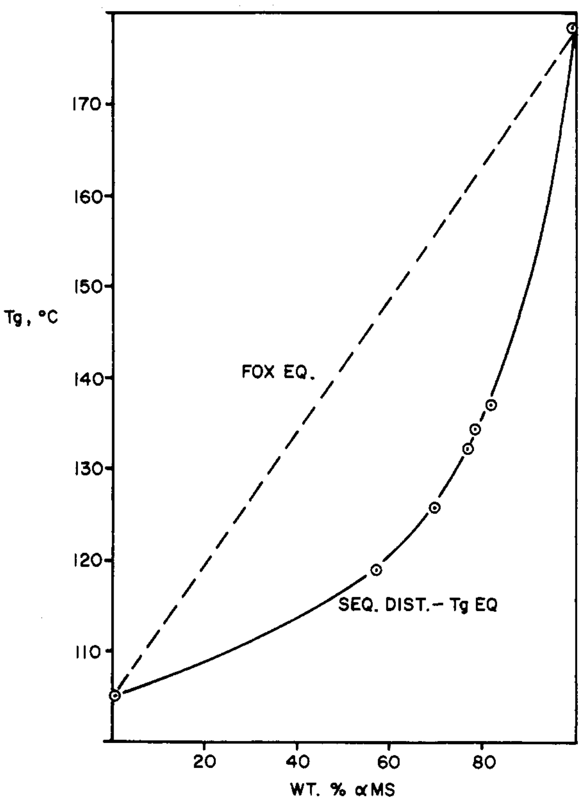

Figure 1. The experimental, sequence distribution predicted, and Fox equation predicted αMS–AN copolymer T_g's *vs.* the weight per cent αMS in αMS–AN copolymers.

The effect of placing a methyl group on an isolated alkyl acrylate or styrene unit does not yield units that have the same T_g as homopolymers of alkyl methacrylate or α-methylstyrene. The high T_g of the alkyl methacrylate or α-methylstyrene homopolymers are due to steric crowding that does not exist in the copolymers reported in this and previous work. An isolated methyl group substituted onto these types of polymer chains contributes a T_g of ~30° to the unit.

There are, of course, many other factors that could influence the T_g's of polymers that have had methyl groups substituted onto them. The methyl group could change the crystallinity as it does in comparing polyethylene *vs.* polypropylene. Methyl substitution could make the unit symmetrical and, therefore, freer to rotate. A methyl group substituted onto polypropylene to yield polyisobutylene seems to produce this type of effect. Polar interactions, tacticity effects and varying degrees of steric crowding by the other substituted groups on the monomers may also influence the T_g's of methyl group substituted copolymers. These factors could result in other than a 30° change in T_g, but do not seem to occur in the systems under consideration.

---

(8) N. W. Johnston and H. J. Harwood, *J. Polym. Sci., Part C,* 22, 591 (1969).

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

The use of the T_g of an alternating copolymer as T_{gAB} in random copolymers is a useful concept and we have used it in several other polymer systems. The value used in this work of 122° for T_{gAB} or the T_g of an αMS–AN dyad worked very well in predicting the T_g's of random copolymers. This value, along with other data, was also used to predict the T_g's of many αMS terpolymers. This work will be published in the near future.

Acknowledgments. The author acknowledges the technical assistance of Mr. J. E. Simborski and the cooperation of Dr. B. L. Joesten of Union Carbide in obtaining the DSC data presented in this work.

Sequence Distributions in Ethylene–Vinyl Acetate Copolymers. I. ^{13}C Nuclear Magnetic Resonance Studies

M. Delfini, A. L. Segre, and F. Conti*

Istituto Chemica-Fisica, University of Rome, Rome, Italy. *Received December 1, 1972*

ABSTRACT: The sequence distribution of ethylene–vinyl acetate copolymers has been studied using ^{13}C nmr spectroscopy. Signal attributions were obtained both by following the rules of Grant and Paul as well as by comparison of spectra of samples of varying composition. Quantitative analysis at low vinyl acetate content are reported. Zeroth-order Markoffian distribution of the monomer units in the copolymer chain was verified. In addition, a ^{13}C spectrum of solid polymer was obtained.

A large number of papers have been published on the applications of nmr to the study of structural problems of homo- and copolymers.[1] One of the most important applications from the theoretical as well as from the technological point of view is the determination of the amount of the relative sequences in copolymers. However, due to the overlapping and consequent distortion of several resonances, no unambiguous determination is possible in some cases. This is the case for ethylene–vinyl acetate copolymers.

The high-resolution proton magnetic resonance (pmr) spectra of these copolymers, ranging from final composition mole fraction $M_E = 0$ to 0.7, have been previously reported.[2] By comparison of the experimental and calculated spectra, a zeroth-order Markoffian monomer distribution in the chain was deduced.[2] The same conclusions have been reached by different authors.[3-5] However, because of the overlapping of the resonance peaks due to different monomer distributions these conclusions cannot be considered unequivocal. Moreover, no results have been reported at lower vinyl acetate content because of the increasing difficulties in observing the different resonance peaks, since the strong ethylene $-CH_2-$ signal covers all the other weak peaks.

Because ^{13}C magnetic resonance (cmr) has several advantages over pmr (spin–spin coupling easily removed by heteronuclear decoupling resonance lines widely spaced, less broadening by dipolar interactions due to the smaller nuclear magnetic moment of the ^{13}C nucleus), we have examined the ^{13}C spectra of ethylene–vinyl acetate copolymers, with the aim of improving previously reported information and obtaining data relative to the copolymers with lower vinyl acetate content. Furthermore we tried also to obtain ^{13}C spectra on solid polymers.

Experimental Section

Materials. Ethylene–vinyl acetate copolymers were obtained by radical copolymerization[6] and the products were used without further purification. Solution viscosities indicated that molecular weights of all copolymers were high. The purity of the compounds as well as their composition were determined by elemental analysis and by both ^{13}C and ^{1}H nmr spectra. The results obtained with the two different methods agreed within ±1%.

All the solvents were spectroscopic grade Merck products and were used without further purification.

All nmr spectra have been run on a Varian XL-100 high-resolution Fourier transform nmr spectrometer operating at 25.2 and 100 MHz for ^{13}C and ^{1}H, respectively. The spectrometer was equipped with a Varian 620 i computer system. The Fourier transform spectra were obtained under the following conditions: acquisition time 0.8 sec; spectral width 5000 Hz; pulse width 60 μsec; data were stored in 8K channels; the pulse interval was 0.8 sec; approximately 3000–5000 transients were collected for each spectrum.

The sample was contained in a 12-mm tube. Chemical shifts were measured from Me_4Si internal reference and are reported in parts per million from $^{13}CS_2$, assumed to be at −194.2 ppm from Me_4Si.

Results and Discussion

In Figures 1–4 are reported ^{13}C spectra of ethylene–vinyl acetate copolymers having different monomer ratios, in solution as well as in the solid state. The different resonances are easily assigned: CH_3 at 173 ppm, CH_2 between 173 and 155 ppm, and CH between 128 and 120 ppm. The carbonyl resonances (not shown in the figures) are between 22 and 25 ppm. In general the variation of the relative monomer ratio (with the exception of very weak signals, which are probably spurious) affects only the intensities of the peaks, not their multiplicity.

Because of different correlation times, the relative intensities of the resonances of the backbone ^{13}C nuclei and of those attributed to side chains (carbonyl and acetyl methyl) may not be reliable for quantitative analysis in the experimental conditions we chose. No effort was made to choose a different sequence of pulses because actually we did not need these data, inasmuch as we chose to carry out the analysis on spectral peaks whose relative intensities can be used without any correction at all. Relative in-

---

[1] F. A. Bovey, "High Resolution NMR of Macromolecules," Academic Press, New York and London, 1972.

[2] J. Schaefer, *J. Phys. Chem.*, **70**, 1975 (1966).

[3] T. K. Wu, *J. Phys. Chem.*, **73**, 1801 (1968).

[4] T. K. Wu, *Macromolecules*, **2**, 520 (1969).

[5] T. K. Wu, *J. Polym. Sci., Part A-2*, **8**, 167 (1970).

[6] (a) W. E. Hanford, U. S. No. 2,396,785 (1942); (b) E. Cernia, *Nuova Chim.*, **4**, 1 (1971).