Glass transition temperatures of copolymer and terpolymer fluoroelastomers

Piergiorgio Bonardelli and Giovanni Moggi
Montefluos, CRS, Via Bonfadini 148, 20138 Milano, Italy

and Antonio Turturro
Istituto di Chimica Industriale, University of Genova, Corso Europa 30, 16132 Genova, Italy

(*Received 5 June 1985; revised 2 September 1985*)

The Fox, Gordon–Taylor–Wood, Johnston and Barton equations have been applied to predict the glass transition temperatures, T_g, of vinylidene fluoride–hexafluoropropene (VDF–HFP) copolymers and VDF–HFP–tetrafluoroethene (TFE) terpolymers. The Fox equation fails to describe the co- and terpolymer systems. The experimental data for VDF–HFP copolymers are well interpreted by the Gordon–Taylor–Wood equation. The Johnston and Barton equations, based on sequence distribution, yield good results for VDF–HFP and VDF–HFP–TFE. The assumptions made about kinetic constants of propagation and the T_g contributions of alternating monomer dyads and polyTFE are also discussed.

(Keywords: glass transition temperature; copolymer; terpolymer; fluoroelastomers; T_g–composition equations)

INTRODUCTION

Polymer–glass transition is one of the most important phenomena in polymers, both technologically and theoretically, in that the glass transition temperature, T_g, represents a point where dramatic changes in polymer properties occur.

In designing polymers for practical uses it is necessary to know exactly at what temperatures physical and mechanical changes take place.

Vinylidene fluoride–hexafluoropropene (VDF–HFP) copolymers and VDF–HFP–tetrafluoroethene (TFE) terpolymers are commercial elastomers (e.g. Viton, Tecnoflon, Daiel and Fluorel), suitable for applications requiring high chemical and thermal resistance. Their use is somewhat limited by stiffening at low temperatures, such as in aerospace applications.

A high content of perfluorinated monomers improves the chemical and thermal inertness of the polymer, but raises its glass transition temperature.

Therefore, it is interesting to study the dependence of T_g on composition to: (1) find the smallest amount of perfluorinated comonomer with corresponding low copolymer and terpolymer T_g and the best chemical and thermal properties; (2) test several equations predicting the T_g of copolymer and terpolymer fluoroelastomers.

Our preliminary results[1,2] have shown that the T_g dependence of VDF–HFP copolymers cannot be accounted for by the Fox equation[3], but is predicted with very good agreement by the sequence distribution equation of Johnston[4].

Attention has been paid to the choice of poly(tetrafluoroethylene) T_g because of its importance in determining the glass transition temperatures of terpolymers.

BACKGROUND

In order to predict the T_g of copolymers and terpolymers, several semiempirical equations have been suggested, starting from different and more or less simple assumptions (e.g. that certain properties of the copolymer or terpolymer are additive combinations of the properties of corresponding homopolymers; that the molecular structure–T_g relation is based on additive contributions of the groups on a mole or weight-fraction basis, etc.)[3-10].

Some of these relations are the following well known Fox[3] and Gordon–Taylor–Wood (GTW)[5,6] equations:

$$\frac{1}{T_g} = \sum_i W_i/T_{g_i} \tag{1}$$

$$T_g = K(T_{g_j} - T_g)W_j/W_i + T_{g_i} \tag{2}$$

where

T_{g_i}, T_{g_j} = T_g of homopolymers i and j

W_i, W_j = weight fractions of the monomer units i, j in the copolymer

K = constant for each copolymer, related to the specific volume of each homopolymer at its T_g (ref. 5)

Di Marzio and Gibbs[7] first pointed out that it was necessary to take into account the effect of adjacent different monomer units on steric and energetic relations in the copolymer backbone.

Later, Barton[10] and Johnston[4] independently described two similar equations, which take into consideration the sequence distribution of the polymer,

0032-3861/86/060905-05$03.00
© 1986 Butterworth & Co. (Publishers) Ltd.

assigning dyads, triads and other sequence distributions their own T_g.

Their treatment can be readily extended to multicomponent copolymer systems; the general forms are:

$$1/T_g = \sum_{i,j} W_i P_{ij} / T_{g_{ij}} \tag{3}$$

$$T_g = \sum_{i,j} n_{i,j} T_{g_{ij}} \tag{4}$$

where

$T_{g_{ij}} = T_g$ contributions of the different monomer dyads, ii, ij, ji, jj

P_{ij} = probability that a growing macromolecule having the free radical on i or j monomer moiety adds i or j monomer unit

$n_{ij} = (N_{ij}\alpha_{ij}) / \sum_{i,j}(N_{ij}\alpha_{ij})$, i.e. mole fraction of ij sequences, N_{ij}, weighted according to the number of rotatable bonds per sequence, α_{ij}

Johnston's approach, equation (3), derives from the Fox equation (1); the Barton equation (4) is an extension of the Gibbs and Di Marzio[7] copolymer T_g theory. If no sequence distribution effect is found, equations (3) and (4) revert back to the Fox and Di Marzio–Gibbs equations, respectively.

We have compared the experimental T_g of copolymer and terpolymer fluoroelastomers with the predictions of equations (1)–(4).

EXPERIMENTAL

Materials

Vinylidene fluoride, hexafluoropropene, and tetrafluoroethene monomers were supplied by Montefluos SpA and were ~99% pure.

VDF–HFP copolymers and VDF–HFP–TFE terpolymers were prepared by semicontinuous emulsion polymerization in a 5 litre stainless steel stirred autoclave at 85°C and 13 atm., in 3.5 litre demineralized water.

The polymerization was done using $3.5\,\mathrm{g\,l^{-1}}$ of ammonium persulphate as free-radical initiator and continuously feeding a gaseous monomer mixture with the same composition as the desired polymer. The initial gas composition in the reactor was adjusted to yield the desired polymer composition, according to the reactivity ratios.

The polymers were coagulated by pouring the latices into an equal volume of a stirred $6\,\mathrm{g\,l^{-1}}$ aluminium sulphate solution, washed with demineralized water and dried at 70°C for 16 h.

Owing to the impossibility of homopolymerizing HFP under normal free radical conditions[11], the composition range that can be experimentally investigated is limited; therefore no copolymer or terpolymer can contain more than 50 mol% HFP.

Later (in formulae) VDF, HFP and TFE are referred to as monomers A, B and C, respectively.

Techniques

Sample composition was determined from ^{19}F n.m.r. spectra, recorded at 188.4 MHz on a Varian XL200 spectrometer, according to literature assignments of chemical shifts[12–14].

Intrinsic viscosity $[\eta]$ measurements were carried out at 30°C in methyl ethyl ketone.

Glass transition temperatures were measured by differential scanning calorimetry, using a Perkin-Elmer DSC-2 calorimeter, with a heating rate of $10\,\mathrm{K\,min^{-1}}$. The intercept of the line of maximum slope with the baseline was assumed to be the T_g.

RESULTS AND DISCUSSION

VDF–HFP copolymers

The T_g of polyVDF and polyHFP homopolymers, used in the calculations, are $T_{g_A} = 227.5\,\mathrm{K}$ and $T_{g_B} = 433\,\mathrm{K}$, respectively. The former value has been measured experimentally and lies between literature values of 233 and 223 K (refs. 15 and 16); the latter is an average between the reported data of 425 K (ref. 16) and 440 K (refs. 17 and 18).

Table 1 lists the calculated and experimental T_g values of VDF–HFP copolymers.

Fox equation. T_g–composition behaviour (*Figure 1*) shows that the Fox equation fails to describe the experimental trend: on increasing the HFP content the copolymer T_g increases less than the Fox equation predicts, as has been reported for many other systems[4] (vinylidene chloride–vinyl chloride, styrene–methyl methacrylate; α-methylstyrene–acrylonitrile, etc.).

Sequence distribution equations. The dyad probabilities P_{ij} used in the Johnston equation were computed from relations involving the reactivity ratios, r_i, and the

Table 1 Experimental and predicted glass transition temperatures of VDF–HFP copolymers

mol%		$[\eta]$	T_g (K)			
VDF	HFP	dl g^{-1}	Experimental	Fox	Johnston	Barton
100	0	—	227.5	—	—	—
95	5	—	234.0	240.5	233.0	232.9
89	11	1.5	240.5	255.1	239.2	238.3
83.7	16.3	1.7	244.0	267.7	243.9	243.0
80.6	19.4	1.7	248.0	274.8	246.4	245.8
77.4	22.6	1.3	250.0	282.3	249.3	248.6
74.2	25.8	1.1	253.5	289.5	251.6	251.5
72.2	27.8	1.0	255.5	294.1	253.6	253.3
66.2	33.8	—	261.3	307.3	259.9	258.2
59.3	40.7	—	267.8	322.0	265.6	264.6

monomer concentrations, $[i]$ (ref. 4):

$$P_{AB}=1/(1+r_A[A]/[B]) \qquad P_{BA}=1/(1+r_B[B]/[A]) \qquad (5)$$
$$P_{AA}=1-P_{AB} \qquad P_{BB}=1-P_{BA}$$

In the gas phase, we have used $r_A=2.45$ and $r_B=0$ for VDF and HFP, respectively. From the latter condition it follows that $P_{BB}=0$; i.e. the B monomer (HFP) does not homopolymerize, as already pointed out, in our reaction system. Equation (3) becomes:

$$1/T_g=(W_AP_{AA}/T_{g_A})+(W_AP_{AB}+W_BP_{BA})/T_{g_{AB}} \qquad (6)$$

The T_g of the alternating copolymer, evaluated by graphical extrapolation of our experimental results, has been assumed as $T_{g_{AB}}=273$ K.

As reported in *Table 1* and illustrated in *Figure 1*, the experimental T_g fit very well the trend predicted by the Johnston equation: the VDF–HFP copolymer T_g are affected by the sequence distribution, similarly to random copolymers, such as α-methylstyrene–acrylonitrile copolymers[4].

The mole fractions of the dyad sequences, N_{ij}, have been obtained from ^{19}F n.m.r. spectra. As HFP cannot homopolymerize $N_{AB}=N_{BA}$ is equal to the mole fraction of HFP in the copolymer, and $N_{AA}=1-2N_{AB}$ (refs. 19 and 20).

Because $P_{BB}=0$, $N_{BB}=0$ and $N_{AB}=N_{BA}$ the Barton equation can be written

$$T_g=n_{AA}T_{g_A}+2n_{AB}T_{g_{AB}} \qquad (7)$$

The predicted results of *Table 1* are in very good agreement with experiment; in other words, by plotting $(T_g-n_{AA}T_{g_A})$ as a function of $2n_{AB}$ we obtain the straight line shown in *Figure 2*. The slope gives $T_{g_{AB}}=275$ K; a value of 273 K was assumed.

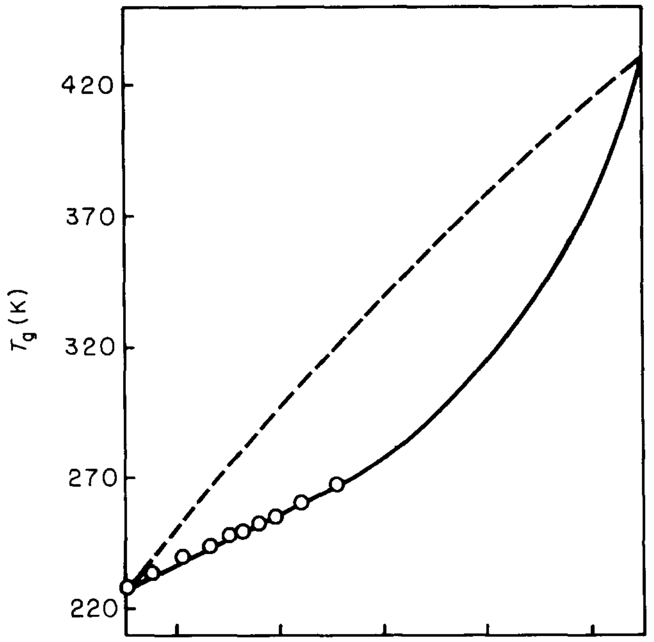

Figure 1 Glass transition temperature, T_g, of VDF–HFP copolymers versus mol% HFP content. (-----), as predicted by Fox equation; (———), as predicted from sequence distribution; ○, experimental values

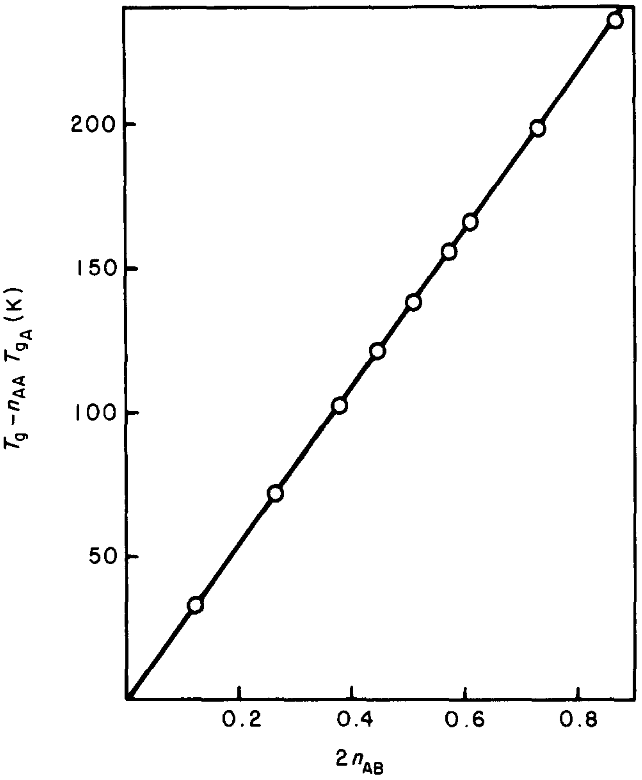

Figure 2 Plot of equation (2) for VDF–HFP copolymers. From slope, $T_{g_{AB}}=275$ K

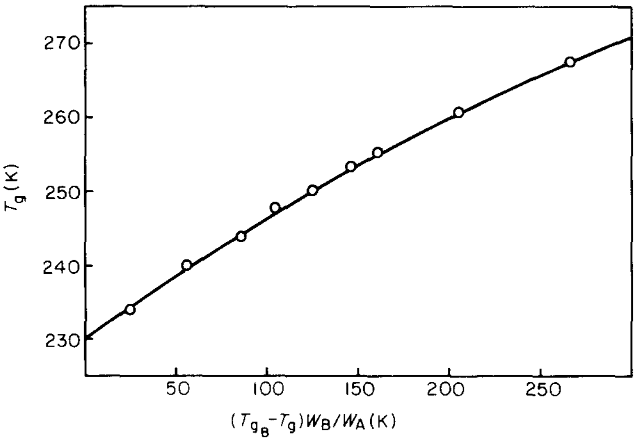

Figure 3 Gordon–Taylor–Wood plot of the VDF–HFP copolymer T_g data

The exact predictions of the sequence distribution relations would indicate that, independently of the type of equation, if the distribution of dyad sequences is considered, they predict very well the experimental T_g of fluoroelastomer copolymers.

Gordon–Taylor–Wood equation

Plotting experimental T_g as a function of $(T_{g_B}-T_g)W_B/W_A$ we obtain the curve of *Figure 3*.

Up to about 30 mol% HFP, the trend is linear and the experimental values are well predicted by the GTW equation.

The intercept $T_g=240$ K is only 2 K higher than the experimental T_g of polyVDF; the linear trend has been found for many different copolymers, e.g. tetrafluoroethene–3,3,3-trifluoropropene copolymers[21].

The value of K determined as the slope of the line, 0.16, is very small compared with the values generally reported in the literature.

VDF–HFP–TFE terpolymers

To analyse the results obtained from VDF–HFP–TFE terpolymers, it was necessary accurately to know the glass transition temperature of poly(tetrafluoroethene). Unfortunately, the value of this temperature has been long controversial and none of the reported experimental values can be preferred. Moreover, the T_g, as determined by extrapolation from copolymers, seems to depend on the chemical nature of the comonomer[22] and, in a few cases, to assume values unknown by direct measurements on the homopolymer[21].

Very recently, Wunderlich *et al.*[23] have shown that the glass transition of poly(tetrafluoroethene) is rather broad, ~160–240 K.

In the light of the rule of constant heat capacity increase per mobile bead, the authors suggest $T_g = 200$ K as an acceptable midpoint for the glass transition of completely amorphous poly(tetrafluoroethene). Using $T_{g_C} = 200$ K, the calculation of terpolymer T_g by the Fox, Johnston and Barton equations leads to values very far from the experimental ones.

In accordance with Simha *et al.*[21], we have used $T_{g_C} = 284$ K, extrapolated from the trend of the T_g of TFE–3,3,3-trifluoropropene copolymers. This last system seems to be the closest to terpolymers containing both the C–H and C–F groups.

Fox equation. Experimental and calculated T_g values for VDF–HFP–TFE terpolymers are listed in *Table 2*.

In this case, too, the Fox equation does not predict the dependence of terpolymer T_g on composition, giving T_g that is always much higher than experimental.

Sequence distribution equations. Dyad probabilities for equation (3) were computed according to Rios and Guillot[24]:

$$P_{Aj} = K_{Aj}[A^{\bullet}][j] \Big/ \sum_{j=\mathrm{A,B,C}} K_{Aj}[A^{\bullet}][j] \qquad (8)$$

where K_{Aj} is the kinetic constant of propagation, $[A^{\bullet}]$ is the concentration of growing free radicals with the unpaired electron on an A monomer unit and $[j]$ is the concentration of monomer j.

From equation (8) P_{Aj} can be deduced as a function of reactivity ratios, r_{Aj}, and monomer concentrations, such that:

$$\begin{aligned} P_{AA} &= r_{AB}[A]/(r_{AB}[A]+[B]+(r_{AB}/r_{AC})[C]) \\ P_{AB} &= [B]/(r_{AB}[A]+[B]+(r_{AB}/r_{AC})[C]) \end{aligned} \qquad (9)$$

The following values of reactivity ratios have been calculated, relative to monomer concentrations in the gas phase:

$$r_{AB} = 2.45 \quad r_{BA} = 0 \quad r_{AC} = 0.23 \quad r_{CA} = 3.73 \quad r_{BC} = 0 \quad r_{CB} = 15.00$$

In the expressions for P_{BA}, P_{BB} and P_{BC} the ratio r_{BA}/r_{BC} is indeterminate because $r_{BA} = r_{BC} = 0$. This is not a problem with P_{BB}, since it is zero, but it prevents P_{BA} and P_{BC} from being calculated.

On the other hand

$$M_{BA}/M_{BC} = (K_{BB}/K_{BA})/(K_{BB}/K_{BC}) = K_{BC}/K_{BA} \qquad (10)$$

i.e. the ratio of the two non-zero kinetic constants for the addition of an HFP-ended macromolecular radical to a TFE and a VDF molecule, respectively. These constants are not known, though there are indications that perfluorinated free radicals add more easily to VDF than to TFE. Tedder, Walton and co-workers[25,26] have reported that at 164°C in gas phase the ratios of the addition rates of $CF_3^{\bullet}$ to ethene, TFE and VDF are $K_{TFE}/K_{C_2H_4} = 0.1$ and $K_{VDF}/K_{C_2H_4} = 0.2$, i.e. the addition of $CF_3^{\bullet}$ to VDF is twice as fast as to TFE.

The differences of reaction conditions and between $CF_3^{\bullet}$ and a macroradical with an unpaired electron on an HFP unit do not allow quantitative extrapolation of these kinetic data to our terpolymerization system, although the reported trend is qualitatively consistent with recent ^{19}F n.m.r. observations[27], according to which the fraction of HFP–TFE sequences in VDF–HFP–TFE terpolymers is very low and until now hardly detectable.

Hence we have considered the best approximation to the actual sequence distribution to be the assumption that HFP–TFE and TFE–HFP sequences are negligible, i.e. $P_{BA} = 1$ and $P_{BC} = 0$.

The sequence distribution equation (3) reduces to:

$$\frac{1}{T_g} = \frac{W_A P_{AA}}{T_g} + \frac{W_A P_{AB} + W_B P_{BA}}{T_{g_{AB}}} + \frac{W_A P_{AC}}{T_{g_{AC}}} + \frac{W_C P_{CC}}{T_{g_C}} \qquad (11)$$

Because $N_{BC} = N_{CB} = 0$, $N_{AB} = N_{BA}$ and $N_{AC} = N_{CA}$, equation (4) becomes:

$$T_g = n_{AA} T_{g_A} + n_{CC} T_{g_C} + 2(n_{AB} T_{g_{AB}} + n_{AC} T_{g_{AC}}) \qquad (12)$$

In this case too the mole fractions of the dyads have been determined by ^{19}F n.m.r. spectroscopy[27].

Assuming that the increment of heat capacity during the glass transition is the same for A (VDF) and C (TFE)

Table 2 Experimental and predicted glass transition temperatures of VDF–HFP–TFE terpolymers

mol%			$[\eta]$ dl g^{-1}	$T_{g_{exp}}$ (K)	T_g (K)		
VDF	HFP	TFE			Fox	Johnston	Barton
35.6	32.8	31.6	—	271.5	318.3	269.5	272.9
49.4	18.4	32.2	—	264.5	289.6	266.7	262.0
55.4	13.0	31.6	1.5	260.5	277.6	264.0	257.2
60.3	24.1	15.6	—	259.5	293.6	261.5	256.6
61.2	16.5	22.3	1.6	255.4	280.4	257.5	255.0
63.8	27.8	8.3	—	258.0	298.3	260.0	255.1
64.3	19.1	16.6	1.4	253.5	283.0	258.8	254.6
71.8	20.7	7.5	1.3	252.0	284.6	257.6	249.0

homopolymer, the T_g of an AC alternating copolymer has been computed according to Couchman[28,29]:

$$T_{g_{AC}} = (T_{g_A} \cdot T_{g_C})^{0.5} \qquad (13)$$

By substituting $T_{g_A} = 227.5$ K and $T_{g_C} = 284$ K, $T_{g_{AC}} = 254.7$ K is obtained.

As shown in *Table 2*, very good agreement is found among the T_g data predicted by equations (11) and (12) and the experimental ones. However Johnston's equation gives results higher by about 2 K for almost all samples while Barton's equation generally predicts T_g values lower by about 3 K. More interestingly, the T_g of terpolymers computed by equations (11) and (12) fit well the experimental data only using $T_{g_C} = 284$ K for completely amorphous polyTFE.

CONCLUSIONS

Synthesis by free radical initiation of vinylidene fluoride-hexafluoropropene (AB) copolymers and vinylidene fluoride-hexafluoropropene-tetrafluoroethene (ABC) terpolymers gives rise to polymers with AA, ABA and AB (BA), AC (CA) sequences in the copolymers and terpolymers, respectively; sequences such as BB or BC (CB) are virtually absent.

Experimentally T_g dependence on composition is not linear and does not follow the Fox equation. The results clearly indicate that the T_g of copolymer and terpolymer fluoroelastomers are affected by the sequence distribution.

This dependence might be explained by considering the strong effects of sequence distribution on T_g that appear with the majority of vinyl type polymers, which are di-α-substituted with large groups.

Copolymerization of the symmetrical repeat unit $-(CH_2{-}CF_2)-$ with $-(CF_2{-}C(CF_3)F)-$ should result in a loss of symmetry and an increase in the T_g contribution of $-(CH_2{-}CF_2)-$ unit. The effect should be less important when $-(CH_2{-}CF_2)-$ and $-(CF_2{-}CF_2)-$ units copolymerize.

As a consequence, positive T_g deviations from linearity

$$T_g > \sum W_i T_{g_i}$$

or the Fox equation

$$1/T_g < \sum W_i / T_{g_i}$$

should occur.

On the contrary, we find negative T_g deviations. This result could probably be due to the reduction, by copolymerization, of polar interactions and/or, mainly, steric hindrance between adjacent monomer units. On increasing the VDF monomer content, the contribution to T_g of hydrogen bonding decreases; moreover, the HFP unit should affect copolymer and terpolymer T_g less than could be predicted, considering the polyHFP T_g, because copolymer and terpolymer chains are free of the steric strain caused by the interactions between $-CF_3$ groups present on alternate carbon atoms of the polyHFP chains.

Therefore it is deduced that the $T_{g_{AB}}$ of alternating VDF–HFP copolymer is about 273 K instead of 340 K, as the Fox equation predicts.

The various experimental points of copolymers fit the GTW plot very well. This could suggest that the constant K is influenced by the sequence distribution, resulting in an average of moderate interactions of all dyads in the copolymer.

Another interesting result concerns the value of T_g for fully amorphous polyTFE. Among several values in literature, the value of 285 K, suggested by Simha *et al.*[21], allows the prediction of T_g of VDF–HFP–TFE terpolymers in very good agreement with experiment.

ACKNOWLEDGEMENTS

The authors thank Mrs Luciana Rosini for the final editing of the manuscript.

REFERENCES

1 Moggi, G., Bonardelli, P. and Turturro, A. *Proc. Inter. Rubber Conf., Paris* 1982, **I**, 9

2 Moggi, G., Bonardelli, P. and Bart, J. C. J. *Polym. Bull.* 1982, **7**, 115

3 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **1**, 123

4 Johnston, N. W. *J. Macromol. Sci., Rev. Macromol. Chem.* 1976, **14B**, 215

5 Wood, L. A. *J. Polym. Sci.* 1958, **28**, 319

6 Gordon, M. and Taylor, J. S. *J. Appl. Chem.* 1952, **2**, 493

7 Di Marzio, E. A. and Gibbs, J. H. *J. Polym. Sci.* 1959, **40**, 121

8 Mandelkern, L., Martin, G. H. and Quinn, F. A. *J. Res. Nat. Bur. Stand.* 1957, **58**, 137

9 Kanig, G. *Kolloid-Z.* 1963, **190**, 1

10 Barton, J. M. *J. Polym. Sci., C* 1970, **30**, 573

11 Schmiegel, W. W. *Kautch. Gummi Kunstst.* 1978, **31**, 177

12 Ferguson, R. C. *J. Am. Chem. Soc.* 1960, **82**, 2416

13 Ferguson, R. C. *Kautch. Gummi Kunstst.* 1965, **18**, 723

14 Moggi, G., Geri, S., Flabbi, L. and Ajroldi, G. *Proc. Int.Rubber, Conf., Venice*, 1979, 1015

15 Brandrup, J. and Immergut, E. H. (Eds.) 'Polymer Handbook', Wiley, New York, 1975, vol. 3, 150

16 Lovinger, A. J. *Dev. Cryst. Polym.* 1982, **1**, 195

17 Brown, D. W. and Wall, E. P. *J. Polym. Sci.* (*A-2*) 1969, **7**, 601

18 Eleuterio, H. S. and Moore, E. P. 'Preprints 2nd Int. Symp. on Fluorine Chemistry', Estes Park, CA, USA, 1962, p. 3

19 Coleman, B. D. and Fox, T. G. *J. Polym. Sci.* 1963, **A1**, 3183

20 Ito, K. and Yamashita, Y. *J. Polym. Sci.* 1965, **A3**, 2165

21 Haldon, R. A., Schell, W. J. and Simha, R. J. *Macromol. Sci.-Phys.* 1967, **B1**(4), 759

22 Brown, D. W. and Wall, L. A. *Polym. Prepr. ACS Div. Polym. Chem.* 1971, **12**(1), 302

23 Lan, S. K., Wesson, J. P. and Wunderlich, B. *Macromolecules* 1984, **17**, 1102

24 Rios, L. and Guillot, J. *Makromol. Chem.* 1980, **181**, 941

25 Cape, J. N., Greig, A. C., Tedder, J. M. and Walton, J. C. *J. Chem. Soc. Faraday* 1975, **71**, 592

26 Tedder, J. M. and Walton, J. C. *Tetrahedron* 1980, **36**, 701

27 Pianca, M. and Bonardelli, P., to be published

28 Couchman, P. R. *Macromolecules* 1980, **13**, 1272

29 Couchman, P. R. *Nature* (*Lond.*) 1982, **298**, 729