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Glass transitions in dimethyl and di-*n*-butyl poly(itaconate ester)s and their copolymers with methyl methacrylate

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Dimethyl and di-*n*-butyl esters of itaconic acid were polymerized and their glass transition temperatures along with those of copolymers obtained with the mentioned ester of itaconic acid with methyl methacrylate have been studied by differential scanning calorimetry. Homopolymer glass transitions decreased as the chain length of ester alkyl groups increased. The glass transition temperatures of copolymer have been analysed as a function of the sequence distribution and their values compared to the theoretical ones derived using Johnson's equation. The values for the supposed transition temperature of the alternating copolymers, T_{g12}, are lower than the averages values expected from the additive contribution of the T_g of the corresponding homopolymers and decreases as the itaconic diester chain lengthens. Comparison of these polymers with the corresponding poly(*n*-alkyl acrylate)s and their copolymers with methyl methacrylate highlighted the similarities in properties. © 1997 Elsevier Science Ltd. All rights reserved.

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INTRODUCTION

Glass transition temperatures of poly(di-*n*-alkyl itaconates), poly(DRI), have been studied largely by Cowie[1–3]. From these studies it follows that T_g values of poly(DRI) decrease monotonically with increasing chain length of di-*n*-alkyl substituents from methyl to hexyl derivates. When the length of the single-bonded carbon atoms of alkyl groups increase from seven to eleven, poly(DRI) shows two apparent glass transitions, T_g^u and T_g^l, where u refers to the higher temperature. T_g^l has been ascribed to the independent micro-Brownian motion of a side chain occurring below the conventional main chain relaxation T_g^u. Itaconate derivates containing *n*-alkyl ester side chain of twelve or more single-bonded carbon atoms displayed a pronounced melting point but no T_g.

Although, some copolymerization and reactivity ratio data of di-*n*-alkyl itaconate with others monomers, like styrene[4–6] or methyl methacrylate[7,8], have been reported, to our knowledge only the thermal stability and glass transition of thermally crosslinkable methyl methacrylate-based copolymers containing monomethyl itaconate or itaconic anhydride as comonomers have been described[9]. Also, random copolymers synthesized from mixtures of dialkylitaconate esters have been studied[10]. Thus, copolymers obtained using dimethyl itaconate as monomer 1, and di-*n*-heptyl itaconate, di-*n*-octyl itaconate or di-*n*-nonyl itaconate as monomer 2 show two transition temperatures. The position of lower transition is approximately composition independent but the inflection diminishes in intensity as concentration of the longer side chain comonomer decreases. The position of the higher transition of the referred copolymers and those of the copolymers obtained from di-*n*-propyl itaconate with di-*n*-octyl itaconate are dependent on the copolymer composition increasing as the content of copolymer became richer in the shorter side chain component[10].

As is well known the incorporation of flexible pendant groups on the main polymer backbone is one of the most useful methods in altering the T_g of the polymers. To do this, copolymerization reactions are one of the generally used ways, since the glass transition is normally spread over a temperature range of several tens of Kelvin according to the nature of the monomers and their kinetics. Recently, we have reported the T_g of methyl methacrylate–methyl acrylate[11] and methyl methacrylate-*n*-butyl acrylate[12] copolymers as a function of alkyl acrylate molar fraction in the copolymer chain. In both cases T_g of copolymers decrease as the molar fraction of alkyl acrylate monomer increase in the copolymer chain being 304.2 K for the methyl methacrylate–methyl acrylate, and 289.7 K for methyl methacrylate–*n*-butyl acrylate, the values for the supposed transition temperature of the alternating copolymer, T_{g12}. As expected, the flexible chain acts as an 'internal' plasticizer for the molecule and produces a general decrease in copolymer T_g as the ester chain lengthens. Considering that poly(DRI) have T_g values which are also dependent of the alkyl length of the substituents, an interesting comparison can be made between methyl methacrylate–*n*-alkyl acrylate and methyl methacrylate–di-*n*-alkyl itaconate copolymers. Thus, this paper focuses on

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the glass transition temperatures of methyl methacrylate–di-*n*-alkyl itaconate copolymers, and discuss the T_g's in terms of copolymer structures, together with the data of methyl methacrylate–*n*-alkyl acrylate copolymers, previously studied.

Furthermore, taking into account the structural resemblance between *n*-alkyl methacrylates, *n*-alkyl acrylates and di-*n*-alkyl itaconates, a study of the effect of the side chain length on the glass transition temperatures of this kind of homopolymer is also described.

EXPERIMENTAL

Homopolymerization and copolymerization

Purification of methyl methacrylate (MMA), dimethyl itaconate (DMI), di-*n*-butyl itaconate (DBI) and 2,2′-azobisisobutyronitrile (AIBN) have been described previously[7,8]. *n*-Butyl methacrylate (BMA) has been purified following a conventional method[13].

Homopolymerization of the mentioned monomers was carried out at 50°C in benzene solution ($3\,mol\,dm^{-3}$) using AIBN ($1.5\times10^{-2}\,mol\,dm^{-3}$) as initiator.

Copolymer samples of MMA with DMI and MMA with DBI were also prepared at 50°C in benzene ($3\,mol\,dm^{-3}$) using AIBN ($1.5\times10^{-2}\,mol\,dm^{-3}$) as initiator. Other experimental details have been given elsewhere[7,8].

Glass transition temperatures

Glass transition temperatures (T_gs) were measured using a Differential Scanning Calorimeter, Perkin Elmer DSC/TA7DX, PC series with a water circulating system for temperatures over ambient, and a Perkin Elmer DSC-2, Data Station 3700 with an Intracooler for low temperatures. The temperature scale was calibrated from the melting point of high purity chemicals (lauric and stearic acids and indium). Samples (~10 mg) weighed to ±0.002 mg with an electronic autobalance (Perkin Elmer AD4) were scanned at $10.0\,K\,min^{-1}$ under dry nitrogen ($20\,cm^3\,min^{-1}$).

The actual value for the glass transition temperature T_g ($T_{1/2}$) has been estimated as the temperature at midpoint of the line drawn between the temperature of intersection of the initial tangent with the tangent drawn through the point of inflection of the trace and the temperature of intersection of the tangent drawn through the point of inflection with the final tangent. The values estimated according to this criterion, when compared with those obtained following some other procedures, may be apparently higher. In our case this is also due in part to the employed rate of heating ($10.0\,K\,min^{-1}$).

RESULTS AND DISCUSSION

Homopolymerization of methyl methacrylate (MMA), *n*-butyl methacrylate (BMA), dimethyl itaconate (DMI) and di-*n*-butyl itaconate (DBI) as well as copolymerization of different monomer mixtures of MMA with DMI and MMA with DBI were carried out at 50°C in benzene using AIBN as initiator. The reactivity ratios were determined as indicated previously[7,8] and their values are given in *Table 1*.

Table 1 Copolymerization reactivity ratios for copolymerization of di-*n*-alkyl itaconates (M_1) with methyl methacrylate (M_2) performed at 50°C in a $3\,mol\,dm^{-3}$ benzene solution

Method	M_1	M_2	r_1	r_2
Kelen–Tüdos	DMI	MMA	0.417 ± 0.009	1.283 ± 0.015
	DBI	MMA	0.717 ± 0.110	1.329 ± 0.090
Tidwell–Mortimer	DMI	MMA	0.419	1.297
	DBI	MMA	0.654	1.254

Table 2 Glass transition temperatures of poly(*n*-alkyl methacrylates), poly(*n*-alkyl acrylates) and poly(di-*n*-alkyl itaconates) determined by d.s.c.

Polymer	T_g (K)	DT[a] (K)
PMMA	396.2	–
PBMA	311.6	84.6
PMA	287.0	109.2
PBA	221.5	174.7
PDMI	371.3	24.9
PDBI	287.8	108.4

[a] DT is the depression temperature measured as the difference between T_g of PMMA and those of the considered homopolymer

The glass transition temperature is the principal transition of amorphous polymer materials and is associated with the onset of long-range segmental motion of the polymer backbone. Many factors influence the temperature location of T_g, but among the most basic is the molecular flexibility which is affected by the type of substituents. However, the variation of magnitude of this effect depends largely on the nature of the side chain with respect to the main chain[14–17].

The T_g values for poly(*n*-alkyl methacrylates) and poly(di-*n*-alkyl itaconates) with methyl and butyl side chain have been measured and its values, along with those for poly(methyl acrylate) and for poly(*n*-butyl acrylate) previously reported[11,12], are collated in *Table 2*. All the considered homopolymers have a lower T_g as the chain length of the ester alkyl groups increases; which is in agreement with the well established criterion that increasing the length of a flexible alkyl side chain brings a monotonic decrease in the value of T_g in a series of vinyl polymeric homologues[18].

Comparison of T_g values for poly(*n*-alkyl methacrylates) and poly(di-*n*-alkyl itaconates) show that the differences between methyl and butyl derivates are around 85 K in both series. However, the poly(di-*n*-alkyl itaconates) have a lower T_g than the poly(*n*-alkyl methacrylates) which have been ascribed to the presence of an additional flexible $-CH_2$ group[19]. On the other hand, the differences between methyl and butyl derivates of the poly(*n*-alkyl acrylates) have a value of 65 K.

The third column of *Table 2* shows the differences between the T_g values of poly(methyl methacrylate) and those of different homopolymers studied in this paper. As can be observed, when α-CH_3 groups of the main chain of poly(methyl methacrylate) are changed for α-hydrogen atoms, i.e. when poly(methyl acrylate) is considered, a depression in T_g of 109 K is noted. However, when α-methyl groups of the main chain of poly(methyl methacrylate) are changed for α-metilencarboxymethyl groups, i.e. when poly(di-*n*-methyl itaconate) is considered, the depression is 25 K. The

relationship between the above mentioned T_g depressions have a value of 4.4, which indicate that the flexibility of the main chain is higher when α-CH_3 groups of poly(methyl methacrylate) are substituted by α-hydrogen atoms than those attained when α-CH_3 groups are substituted by α-CH_2–$COOCH_3$ groups. In a similar way, as can be observed in *Table 2*, T_g for poly(butyl acrylate) and T_g for poly(di-*n*-butyl itaconate) have depressions with respect to those of poly(methyl methacrylate) of 175 and 108 K, respectively, which show that the butyl derivates have a T_g decrease with respect to the T_g of poly(methyl methacrylate) higher than the methyl ones. However, the relationship between the T_g decrease of poly(butyl acrylate) and the T_g decrease of poly(di-*n*-butylitaconate) have a value of 1.6, which pointed out a flexibilization with respect to poly(methyl methacrylate) slightly higher for poly(*n*-butyl acrylate) than those obtained for poly(di-*n*-butyl itaconate).

Physical properties of a copolymer are fundamentally determined by its sequence as well as chemical structure and composition. The simplest relationships which describes the effect of composition of involved monomer units of a linear copolymer on T_g are the Di Marzio–Gibbs and Fox equations[20,21] which often give unsatisfactory results. However, there are some other equations which gives very similar theoretical curves in very good agreement with the experimental results[11,22]. Among them the Gordon–Taylor–Wood equation[23,24], which is based on the 'free volume' concept, or the Johnston[25], Barton[26], and Couchman[27] equations, which predict the T_g in terms of the monomer unit sequences (diad sequences) in the copolymer. We use the Johnston equation below.

Johnston's[25] equation assumes that M_1M_1, M_1M_2 or M_2M_1 and M_2M_2 diads have their own T_g, the copolymer T_g being described by

$$\frac{1}{T_g} = \frac{w_1 P_{11}}{T_{g_{11}}} + \frac{w_2 P_{22}}{T_{g_{22}}} + \frac{w_1 P_{12} + w_2 P_{21}}{T_{g_{12}}}$$

where w_1 and w_2 are the weight fraction of two monomer units M_1 and M_2. $T_{g_{11}}$, $T_{g_{22}}$ and $T_{g_{12}}$ denote the T_g contribution of the M_1M_1, M_2M_2 and M_1M_2 or M_2M_1 diads in the copolymer, and can be substituted by the T_g of M_1 homopolymer, M_2 homopolymer and the supposed glass transition temperature for the alternating M_1M_2 copolymer, respectively. P_{11}, P_{22} and P_{12} or P_{21} indicate the probabilities of finding M_1M_1, M_2M_2 and M_1M_2 or M_2M_1 diads in the copolymer chain, respectively, and can be calculated by using the monomer feed compositions and monomer reactivity ratios[28].

T_g values for DMI–MMA and DBI–MMA copolymers were taken as described before from the heating traces, averaged for two repeated experiments and shown in *Tables 3* and *4*, respectively.

T_{g12} for DMI–MMA and DBI–MMA copolymers are unknown, but they have been estimated from our own experimental data of involved homopolymers and those of a series of DMI–MMA and DBI–MMA copolymers obtained at low conversions using a linearized form of the Johnston equation[25]. For both system experimental data yields, as can be seen in *Figure 1*, straight lines are obtained from which the values are collated in *Table 5*. From the T_{g12} values indicated in *Table 5*, it is clear that the higher the side chain of the itaconic diester in the system, the lower the $T_{g_{12}}$ value. A similar effect on the $T_{g_{12}}$ values is observed when methyl methacrylate–*n*-alkyl acrylate systems are considered. Curves of *Figure 2* have been drawn according to the Johnston equation[25] considering both the reactivity ratios and the $T_{g_{12}}$ values.

Table 3 Methyl methacrylate molar fraction in the copolymer (F_{MMA}) and values for the glass transition temperatures of DMI–MMA copolymers

F_{MMA} copolymer	T_g (K)	F_{MMA} copolymer	T_g (K)
0.00_0	371.3	0.62_6	382.9
0.27_8	370.8	0.62_6	383.3
0.31_0	370.1	0.65_9	383.3
0.31_6	368.5	0.66_0	384.6
0.31_8	372.8	0.67_3	384.8
0.33_8	372.8	0.67_8	385.3
0.34_7	372.7	0.71_6	387.0
0.35_0	372.8	0.72_1	385.3
0.36_1	373.1	0.72_3	387.7
0.39_3	370.7	0.73_2	387.8
0.39_4	371.5	0.83_2	389.6
0.39_5	373.8	0.83_4	392.2
0.39_6	374.2	0.83_8	394.7
0.61_3	383.2	0.84_6	392.6
0.62_5	383.3	1.00_0	396.2

Table 4 Methyl methacrylate molar fraction in the copolymer (F_{MMA}) and glass transition temperatures of DBI–MMA copolymers

F_{MMA} copolymer	T_g (K)	F_{MMA} copolymer	T_g (K)
0.00_0	287.8	0.62_3	326.6
0.26_8	305.8	0.74_1	341.0
0.37_2	308.0	0.75_4	343.8
0.37_7	311.7	0.75_8	353.9
0.48_8	315.1	0.83_5	353.1
0.54_1	319.5	0.94_4	365.9
0.58_4	331.2	0.95_7	370.8
0.58_9	320.8	0.97_4	372.0
0.61_8	324.1	1.00_0	396.2

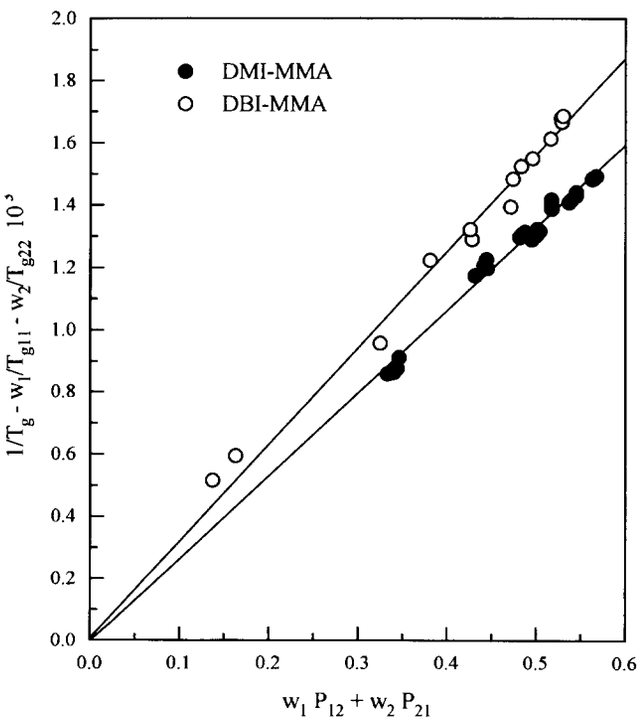

Figure 1 Plots of the glass transition temperatures of copolymers according to the linearized expression of Johnston[25]

Table 5 Glass transition alternating diad M_1M_2 or M_2M_1 and average value of the homopolymers glass transitions

Copolymer	$T_{g_{12}}$ (K)	$\bar{T}_g$ [a] (K)	ΔT_g [b] (K)
MA–MMA	304.2	348.7	44.5
BA–MMA	289.7	308.9	19.2
DMI–MMA	375.1	383.8	8.7
DBI–MMA	326.8	342.0	15.2

[a] $\bar{T}_g$ is the average $\bar{T}_g = (T_{g_{11}} + T_{g_{22}})/2$
[b] $\Delta T_g = \bar{T}_g - T_{g_{12}}$

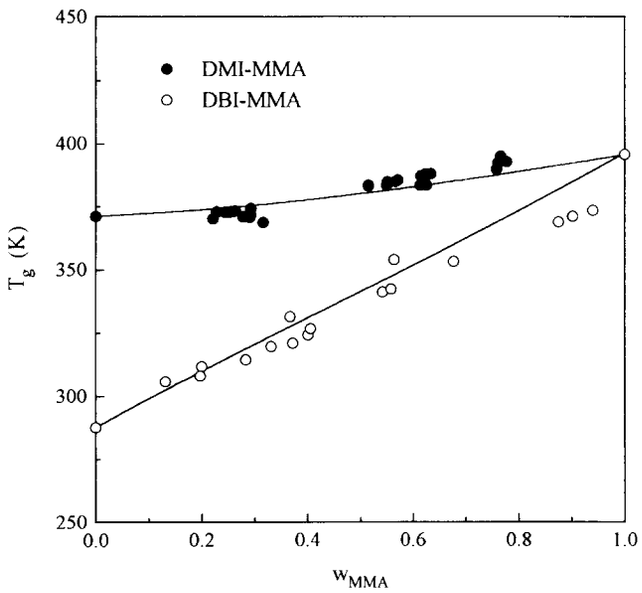

Figure 2 Glass transition temperature of copolymers as a function of methyl methacrylate weight fraction in the copolymer chain

The good agreement between experimental and theoretical values indicates that the Johnston equation[25] and the terminal model through reactivity ratios may be used to describe the dependence between the experimental T_g of DMI–MMA as well as DBI–MMA copolymers and their sequence distribution.

Although, in *Figure 2*, for DBI–MMA copolymers with weight fractions of MMA higher than 0.85 it seems that the T_g values deviate from the predictions of the Johnston equation[25]. In a previous paper[29] we have extended the glass transition temperature data obtained at low conversion to the copolymer obtained at high conversion. In the mentioned paper[29] it has been observed that a good agreement between experimental values for the glass transition temperatures of copolymer obtained in a wide range of conversions and monomer feed compositions with those theoretically calculated from Johnston's equation, using the $T_{g_{12}}$ estimated in this paper, and a step-function to predict the copolymer composition drift over the copolymerization course.

However, Hirooka and Kato[30] have observed that the T_g for diads, $T_{g_{12}}$, calculated from the T_g of a series of copolymers of varied compositions, does not always correspond with that of the chemical synthesized alternating copolymer[31]. Hirooka *et al.*[30,31] concluded that the deviation of the T_g of an alternating copolymer from the T_g of a statistical 1/1 copolymer depends on the type of T_g–composition relationship of the statistical copolymer involved. T_g of an alternating copolymer is higher, lower or similar to that T_g estimated from T_g-sequence distribution when the T_g–composition curve for statistical copolymer is convex, concave or linear, respectively.

In order to explain such deviations, Tonelli[32] has used the conformational entropy as a characterizing parameter for the polymer intramolecular chain flexibility. He pointed out that the positive, negative or no deviations from bulk additive, namely, $T_{g_{12}}$ estimated from T_g-sequence distribution behaviour, are produced when the conformational entropy for a given copolymer chain is lower, higher or similar, respectively, to the weighted sum entropies calculated for the constituent homopolymer chains.

On the other hand, the T_g of the polymer is related to the chain flexibility and this parameter is, to a large extent, a reflection of the rotational barrier about the bond linking two monomer units.

In copolymers obtained in the free radical polymerization of di-*n*-alkyl itaconates (M_1) and methyl methacrylate (M_2), there are chains which have M_1-M_1, M_2-M_2, M_1-M_2 or M_2-M_1 links. Depending on the rotational barrier of the heterolink bond being similar, higher or lower that the averaged rotational barrier of the homolink bonds, the copolymer T_g–composition behaviour will be linear or show positive or negative deviations from linearity[33]. Hirooka and Kato[30] have proposed that the difference between the average $\bar{T}_g = (T_{g_{11}} + T_{g_{22}})/2$ and the supposed transition temperature of the alternating copolymer $T_{g_{12}}$ may be regarded as a measure of the heterolink stiffness.

Table 5 gives the average $\bar{T}_g$ corresponding to both equimolecular random DRI–MMA copolymers. In both cases the value of $T_{g_{12}}$ obtained using the Johnston equation[25] is lower than that of the averages $\bar{T}_g$ corresponding to respective equimolecular random copolymers, which indicates that the studied systems have a heterolink stiffness slightly lower that the average of the homopolymer links. Nevertheless, it is difficult to distinguish visually the negative deviations from the linearity expected in the copolymer T_g–composition behaviour drawn in *Figure 2* although values shown in *Table 5* are operating on the reduction of heterolink stiffness. Notwithstanding, the cause of this effect is not clear since chain flexibility not only depends on the rotational barrier but also on the chain packing, side chain stiffness, dipole interactions, etc.

From the point of view of the glass transition temperature, MA–MMA and DMI–MMA systems can be considered as chains of poly(methyl methacrylate) that become increasingly substituted with H atoms, or $-CH_2-COOCH_3$ groups, at the α position as methyl acrylate, or dimethyl itaconate, comonomers in the copolymer increase. If we consider, in agreement with Hirooka and Kato[30], that the difference between the average $\bar{T}_g$ and the supposed transition temperature of the alternating copolymer $T_{g_{12}}$ may be regarded as a measure of heterolink stiffness (ΔT_g values shown in *Table 5*), the MA–MMA link has five times lower stiffness than that of the DMI–MMA link. In a similar way, heterolink stiffness of BA–MMA is 1.3 times lower than heterolink stiffness of DBI–MMA. Therefore, heterolink stiffness for methyl methacrylate-*n*-alkyl acrylates and for methyl methacrylate-di-*n*-alkyl itaconate diads are in agreement with the observed changes in

backbone flexibility when poly(*n*-alkyl acrylate)s and poly(di-*n*-alkyl itaconate)s are compared with the backbone flexibility of poly(methyl methacrylate).

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REFERENCES

1 Cowie, J. M. G. *Pure Appl. Chem.* 1979, **51,** 2331
2 Cowie, J. M. G. *Polym. Eng. Sci.* 1979, **19,** 709
3 Cowie, J. M. G. *J. Macromol. Sci. Phys.* 1980, **B-18,** 563
4 Otsu, T., Kamagishi, K. and Joshioka, M. *Macromolecules* 1992, **25,** 2713
5 Otsu, T., Wanabe, H., Yang, J. Z. and Joshioka, M. *Makromol. Chem. Macromol. Symp.* 1992, **63,** 87
6 Otsu, T. and Wanabe, H. *Eur. Polym. J.* 1993, **29,** 167
7 Madruga, E. L. and Fernández-García, M. *Polymer* 1994, **35,** 4437
8 Fernández-García, M., Cuervo-Rodriguez, R. and Madruga, E. L. *Polymer* 1996, **37,** 263
9 Miles, A. F. and Cowie, J. M. G. *Eur. Polym. J.* 1991, **27,** 165
10 Cowie, J. M. G., McEven, I. J. and Yazdani-Padran, M. *Macromolecules* 1983, **16,** 1151
11 Fernández-García, M., López-González, M. M. C., Barrales-Rienda, J. M., Madruga, E. L. and Arias, C. *J. Polym. Sci. Polym. Phys.* 1994, **32,** 1191
12 Fernández-García, M. Thesis, Madrid, 1995
13 Stickler, M. *Makromol. Chem. Macromol. Symp.* 1987, **10/11,** 17
14 Halden, R. A., Schell, W. J. and Shima, R. *J. Macromol. Sci.* 1967, **B-1,** 759
15 Hoff, E. A. W., Robinson, D. W. and Willbourn, A. H. *J. Polym. Sci.* 1955, **18,** 161
16 Rogers, S. S. and Mandelker, L. *J. Phys. Chem.* 1957, **61,** 985
17 Bandrup, J. and Immergut, E. H. 'Polymer Handbook', 2nd Edn, Wiley-Interscience, New York, 1975
18 Reimschussel, H. K. *J. Polym. Sci. Polym. Chem. Ed.* 1979, **17,** 2447
19 Cowie, J. M. G., Henshall, S. A. E., McEven, I. J. and Velickovic, J. *Polymer* 1977, **18,** 612
20 Di Marzio, E. A. and Gibbs, J. H. *J. Polym. Sci.* 1959, **40,** 121
21 Fox, T. G. *Bull. Am. Phys. Soc.* 1956, **1,** 123
22 Guillot, J. and Emilie, B. *Makromol. Chem. Rapid. Commun.* 1991, **12,** 117
23 Gordon, M. and Taylor, J. S. *J. Appl. Chem.* 1952, **2,** 493
24 Wood, L. A. *J. Polym. Sci.* 1958, **28,** 319
25 Johnston, N. W. *J. Macromol. Sci. Rev. Macromol. Chem.* 1976, **C-14,** 215
26 Barton, J. M. *J. Polym. Sci.* 1970, **30,** 573
27 Couchman, P. R. *Macromolecules* 1982, **15,** 770
28 Harwood, H. J. and Ritchey, W.M. *J. Polym. Sci. B* 1964, **2,** 601
29 Madruga, E. L. and Fernández-García, M. *Eur. Polym. J.* 1995, **31,** 1103
30 Hirooka, M. and Kato, T. *J. Polym. Sci. Polym. Lett. Ed.* 1974, **12,** 31
31 Hirooka, M., Jabunchi, H., Iseki, J. and Nakai, Y. *J. Polym. Sci. A1* 1968, **6,** 1381
32 Tonelli, A. *Macromolecules* 1977, **10,** 716
33 McEven, I. J. and Johnston, A. F. 'Alternating Copolymer' (Ed. J. M. Cowie), Plenum Press, New York, 1985