Chain entanglement in homopolymers, copolymers and terpolymers of methyl methacrylate, styrene and *N*-phenylmaleimide*

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Chain entanglement in poly(methyl methacrylate), polystyrene, poly(*N*-phenylmaleimide), poly(methyl methacrylate-*stat*-styrene), poly(methyl methacrylate-*stat*-*N*-phenylmaleimide) and poly(methyl methacrylate-*stat*-styrene-*stat*-*N*-phenylmaleimide) is studied in the melt by dynamic viscoelastic spectroscopy. It is shown that the plateau modulus is equal to the storage modulus at the minimum of loss tangent. The plateau modulus and the entanglement molecular weight are found to obey the geometric mean relationship with respect to composition, i.e. $\log G_N^0 = \sum v_j \log G_{N_j}^0$ and $\log M_e = \sum v_j \log M_{e_j}$, where G_N^0 is the plateau modulus, M_e the molecular weight between entanglement points, v_j the volume fraction of comonomer j, $G_{N_j}^0$ the plateau modulus for the homopolymer of j and M_{e_j} the entanglement molecular weight for the homopolymer of j. The G_N^0 and M_e of homopolymers and copolymers may also be predicted by group additivity method.

(Keywords: chain entanglement; dynamic viscoelastic spectroscopy; plateau modulus; storage modulus; loss tangent)

INTRODUCTION

Recently, we studied the chain entanglement behaviour in miscible blends of polymers[1-3]. It was found that, in θ blends (in which the Flory–Huggins interaction parameter $\chi = 0$), the entanglement density (i.e. the number of entanglement junctions per unit volume) is linearly additive with respect to the volume fraction of blend composition. However, in blends with $\chi < 0$, the entanglement density was found to be smaller than linear additivity. The negative deviation increases with increasing strength of interchain interaction (i.e. increasing $-\chi$).

The reduced chain entanglement in miscible blends arises because specific interchain interactions tend to cause certain chain segments to spatially align in such a way so that interchain interactions can occur[1-4]. Such alignment tends to locally stiffen these chain segments, reduce local chain tortuosity and thus result in reduced chain entanglement[1-4]. Interestingly, this observation is consistent with recent findings of possible local ordering in miscible blends by Saito and co-workers[5] in miscible blends of poly(methyl methacrylate) (PMMA) and poly(vinylidene fluoride) studied by polarized light scattering, by Rao and co-workers[6] in blends of PMMA and polyoxyethylene studied by i.r. spectroscopy, and by Zhao and co-workers[7] in the same blends studied by mechanical stress relaxation.

In this work, we study the chain entanglement in homopolymers, copolymers and terpolymers of methyl methacrylate (MMA), styrene (S) and *N*-phenylmaleimide (ϕMI).

EXPERIMENTAL

Materials

Three homopolymers, PMMA, polystyrene (PS) and poly(*N*-phenylmaleimide) (PϕMI), two series of copolymers, poly(methyl methacrylate-*stat*-styrene) (PMMA-S) and poly(methyl methacrylate-*stat*-*N*-phenylmaleimide) (PMMA-ϕMI), and one series of terpolymers, poly(methyl methacrylate-*stat*-styrene-*stat*-*N*-phenylmaleimide) (PMMA-S-ϕMI), were studied. The first member of the comonomers is designated as comonomer 1, the second member as comonomer 2, and the third member as comonomer 3. Specifically, in PMMA-S, comonomer 1 is MMA, and comonomer 2 is S. In PMMA-ϕMI, comonomer 1 is MMA, and comonomer 2 is ϕMI. In PMMA-S-ϕMI, comonomer 1 is MMA, comonomer 2 is S, and comonomer 3 is ϕMI. *Tables 1–4* list all the polymers used.

All polymer samples (except the few commercial products indicated) were prepared by aqueous emulsion polymerization at 65–85°C, using sodium laurylsulphonate as the emulsifier, potassium persulphate/sodium bisulphate as the initiator (0.65 mol% monomer) and alkylmercaptan as the chain transfer agent (0–0.36 mol% monomer). The resulting polymer was precipitated with methanol and magnesium sulphate, filtered and washed repeatedly with methanol and water, and then dried at 90°C in vacuum under nitrogen bleed.

The compositions were determined by n.m.r. and elemental analysis of nitrogen for PMMA-ϕMI copolymers, and by elemental analysis of C, H, N and O for PMMA-S-ϕMI terpolymers. On the other hand, the compositions for PMMA-S copolymers were taken to be equal to the monomer feed.

The glass transition temperature (T_g) was character-

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Table 1 Plateau modulus G_N^0 of PMMA

M_w			G_N^0 (dyn cm^{-2})[a]		Tacticity (triads)			
(kg mol^{-1})	M_w/M_n	T (°C)	$(\tan\delta)_{min}$	G'' integral	*mm*	*mr*	*rr*	Footnote
102.0	1.10	180	4.0×10^6	4.3×10^6	–	–	–	*b*
115.0	1.11	190	4.2×10^6	4.3×10^6	0.018	0.418	0.564	*b*
123.0	1.75	180	4.6×10^6	–	0.039	0.372	0.589	*b,c*
95.3	1.88	145	4.3×10^6	–	–	–	–	*b,d*
96.4	1.90	160	4.2×10^6	–	0.101	0.465	0.434	*b*
84.4	1.91	144	4.0×10^6	–	0.141	0.449	0.410	*b*
93.3	2.01	157	4.4×10^6	–	–	–	–	*b*
88.8	2.23	155	4.2×10^6	–	–	–	–	*b*
121.0	2.30	150	4.2×10^6	–	–	–	–	*b*
164.0	2.37	175	4.1×10^6	–	–	–	–	*b*
92.7	2.49	180	4.6×10^6	–	0.017	0.243	0.739	*e*
2860.0	3.91	180	4.3×10^6	–	0.042	0.374	0.584	*b*

[a] The average value of G_N^0 by $(\tan\delta)_{min}$ is $(4.25 \pm 0.19) \times 10^6$ dyn cm^{-2}
[b] Free radical polymerized
[c] Containing 1% by weight of vinyl acetate comonomer
[d] Containing 3.5% by weight of methyl acrylate comonomer
[e] A commercial syndiotactic-rich sample

Table 2 Summary for PMMA-S copolymers

w_2	v_2	M_w (kg mol^{-1})	M_w/M_n	G_N^0 (dyn cm^{-2})	T (°C)[a]	$\rho(T)$[b] (g cm^{-3})	M_e (kg mol^{-1})	Sample source
0.00	0.000	–	–	4.2×10^6	180	1.095	9.82	*Table 1*
0.10	0.113	300	2.73	3.8×10^6	200	1.081	11.2	This work
0.25	0.273	375	2.87	3.2×10^6	195	1.062	13.1	This work
0.40	0.429	275	2.38	2.9×10^6	170	1.062	13.7	RPC-100[c]
0.70	0.725	191	2.28	2.1×10^6	160	1.030	17.6	NAS[c]
0.80	0.818	288	2.56	1.8×10^6	160	1.018	20.0	P-359[c]
0.90	0.910	320	2.83	1.6×10^6	170	1.001	22.5	CIE[c]
1.00	1.000	–	–	1.5×10^6	180	0.984	24.7	This work

[a] Temperature at which G_N^0 was measured
[b] Melt density at temperature T
[c] Commercial samples from Polysar Richardson Polymer Corporation

Table 3 Summary for PMMA-ϕMI copolymers

w_2	v_2	M_w (kg mol^{-1})	M_w/M_n	G_N^0 (dyn cm^{-2})	T (°C)	$\rho(T)$ (g cm^{-3})	M_e (kg mol^{-1})
0.000	0.000	863	3.23	4.2×10^6	180	1.10	9.82
0.075	0.064	188	2.96	3.4×10^6	210	1.09	12.8
0.078	0.066	605	2.96	3.8×10^6	225	1.08	11.8
0.091	0.077	719	3.11	3.1×10^6	180	1.10	15.4
0.163	0.140	165	2.43	2.4×10^6	220	1.10	18.9
0.163	0.140	133	1.91	2.8×10^6	225	1.10	16.3
0.171	0.147	147	2.11	2.4×10^6	220	1.11	18.9
0.173	0.149	780	4.18	2.6×10^6	250	1.09	18.2
0.175	0.151	342	2.86	2.7×10^6	220	1.11	16.8
0.250	0.218	95	2.25	2.1×10^6	225	1.12	29.1
0.263	0.230	309	3.10	2.0×10^6	225	1.13	23.3
0.271	0.237	540	3.19	1.9×10^6	220	1.13	24.4
0.288	0.253	317	2.87	1.8×10^6	235	1.14	26.1
0.348	0.309	244	2.04	1.3×10^6	230	1.15	37.0
0.361	0.321	164	1.41	1.2×10^6	225	1.16	40.0
0.446	0.403	323	2.70	9.6×10^5	240	1.18	52.6
0.513	0.469	305	2.40	8.3×10^5	240	1.21	62.2
0.635	0.593	757	4.25	6.3×10^5	260	1.26	89.4
1.000	1.000	–	–	1.4×10^5[a]	280	1.10	384.2

[a] Calculated by group additivity (see text)

Table 4 Summary for PMMA-S-ϕMI terpolymers

Nominal mole ratio MMA/S/ϕMI	Actual volume ratio MMA/S/ϕMI	M_w (kg mol^{-1})	M_w/M_n	T_g (°C)	G_N^0 (dyn cm^{-2}) Measured	G_N^0 (dyn cm^{-2}) Calculated equation (22)^a
80/10/10	74.1/11.4/14.5	148	2.25	137	2.2×10^6	2.3×10^6
70/15/15	60.4/17.4/22.2	183	2.61	147	1.6×10^6	1.6×10^6
64/18/18	57.1/16.7/26.2	305	1.97	159	1.3×10^6	1.4×10^6
60/20/20	50.9/20.9/28.2	236	2.02	159	1.3×10^6	1.3×10^6
36/32/32	34.0/29.6/36.4	215	2.33	187	9.3×10^5	9.0×10^5

^{a}The G_N^0 values used for homopolymers in equation (22) are 4.2×10^6 dyn cm^{-2} for PMMA, 1.5×10^6 dyn cm^{-2} for PS and 1.4×10^5 dyn cm^{-2} for PϕMI

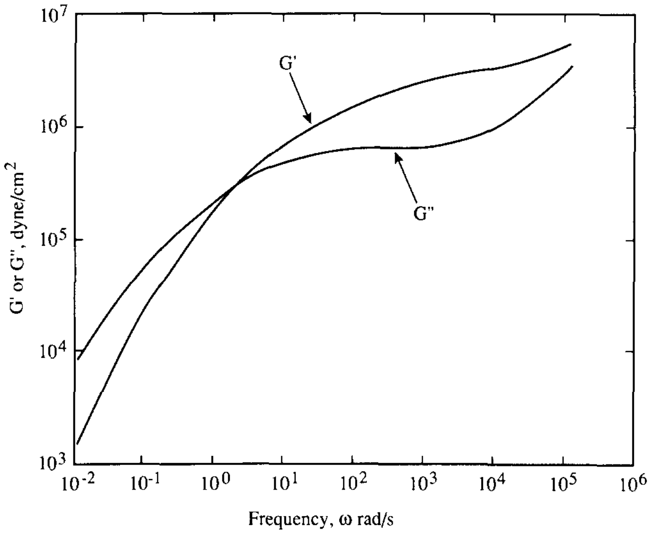

Figure 1 Dynamic modulus master curves for PMMA-S (0.571/0.429 by volume) at 180°C

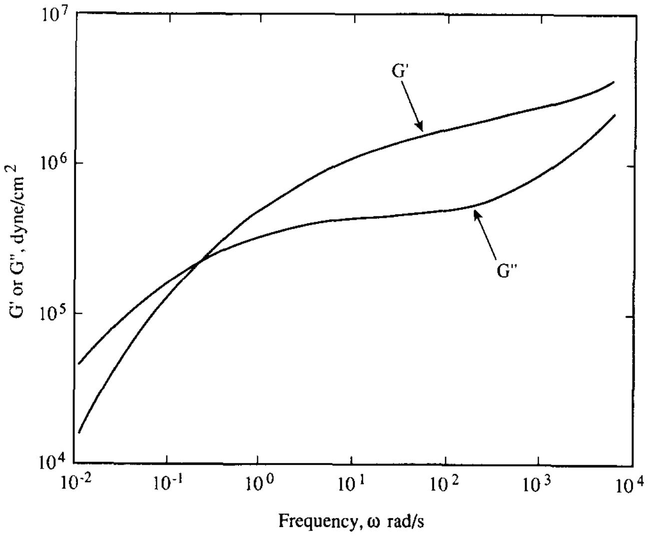

Figure 2 Dynamic modulus curves for PMMA-ϕMI (0.747/0.253 by volume) at 250°C

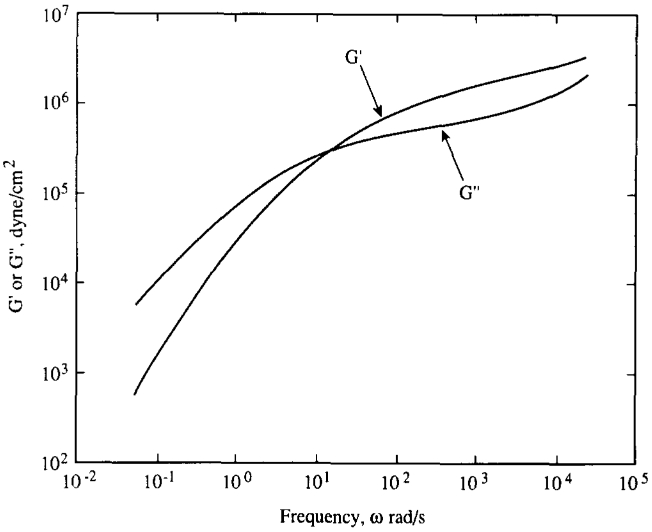

Figure 3 Dynamic modulus curves for PMMA-S-ϕMI (0.509/0.209/0.282 by volume) at 240°C

ized by d.s.c. at 20°C min^{-1} (taken as the midpoint of the step increase in heat capacity). The M_w (weight-average) and M_n (number-average) molecular weights were determined by size exclusion chromatography (tetrahydrofuran at 80°C, calibrated with PMMA standards) and membrane osmometry in hexafluoroisopropanol. The tacticities of PMMA (triad fractions, m = meso, r = racemic) were determined by n.m.r. The results are summarized in *Tables 1–4*.

Dynamic viscoelastic spectroscopy

The plateau modulus (G_N^0) was determined from a linear viscoelastic dynamic modulus spectrum, measured by sinusoidal oscillation with small strains (generally 0.5–5%) as a function of frequency and temperature in the melt, using a Rheometrics mechanical spectrometer system IV. All dynamic spectra could be time–temperature superimposed.

Three typical linear viscoelastic dynamic–modulus spectra are shown in *Figure 1* for PMMA-S (at 180°C with 0.571 and 0.429 volume fractions of MMA and S, respectively), in *Figure 2* for PMMA-ϕMI (at 250°C with 0.747 and 0.253 volume fractions of MMA and ϕMI, respectively), and in *Figure 3* for PMMA-S-ϕMI (at 240°C with 0.509, 0.209 and 0.282 volume fractions of MMA, S and ϕMI, respectively).

The storage modulus (G') at the frequency where tan δ is at a minimum in the plateau zone is G_N^0, i.e.

$$G_N^0 = (G')_{\tan\delta\to\text{minimum}} \qquad (1)$$

This method has been used previously[4,8,9]. We verify its validity herein (see later). The G_N^0 value thus determined is usually reproducible within 10%, and is independent of

Table 5 Structural constants for monomeric units MMA, S and ϕMI

Unit	M_r (g mol^{-1})	n_r	n_v	M_v (g mol^{-1})	$\langle l_v \rangle$ (Å)	$\langle l_v^2 \rangle$ (Å^2)	L_r (g$^{1/4}$ cm$^{3/2}$ mol$^{-3/4}$)	ρ_r at 25°C (g cm^{-3})[a]
MMA	100	2	2	50	1.53	2.341	24.25	1.13
S	104	2	2	52	1.53	2.341	30.15	0.994
ϕMI	173	2	1	173	2.51	6.285	83.6	1.35

[a] Rubbery densities ρ_r are estimated by additivity of molar atomic volumes listed by van Krevelen[11]. These are used to calculate the volume fractions from the weight fractions

Table 6 Group constants K_i for molar stiffness function[a]

Group	K_i (g$^{1/4}$ cm$^{3/2}$ mol$^{-3/4}$)
CH_3–	3.55
–CH_2–	2.35
>CH–	1.15
>C<	0
–C(=O)–O– (acrylic)	6.4
–(*N*-phenylmaleimide)–	75.2

[a] All values are from van Krevelen[11], except for *N*-phenylmaleimide which is determined in this work

molecular weight and distribution (polydispersity), as long as the fractions with molecular weights lower than the entanglement value are negligible.

When there are appreciable amounts of fractions having molecular weights below the entanglement value, the G' value at the minimum of tan δ is an apparent G_N^0 value. The true G_N^0 value is greater than the apparent value, and can be obtained by[10]:

$$G_N^0 = (G_N^0)_a / v_p^2 \qquad (2)$$

where $(G_N^0)_a$ is the apparent plateau modulus (i.e. the G' value at the minimum tan δ), and v_p the volume fraction of the polymer having molecular weights above the entanglement value.

The entanglement molecular weight M_e is calculated by

$$M_e = \rho RT / G_N^0 \qquad (3)$$

where ρ is the mass density at temperature T at which the plateau modulus G_N^0 was measured and R is the gas constant. The density ρ was measured by dilatometry.

The volume fraction v_j was calculated from the weight fraction w_j by using rubbery molar atomic volumes listed by van Krevelen[11]. *Tables 5* and *6* list some structural constants.

RESULTS AND DISCUSSION

Glass transition temperature

Each PMMA-ϕMI copolymer has a single T_g, plotted in *Figure 4*. The data appear to fit the Fox equation[12], i.e.

$$1/T_g = w_1/T_{g_1} + w_2/T_{g_2} \qquad (4)$$

where w_j is the weight fraction of comonomer j and T_{g_j} the glass transition temperature of the homopolymer of j. Least-squares regression gives $T_g = 537$ K for the homopolymer of ϕMI.

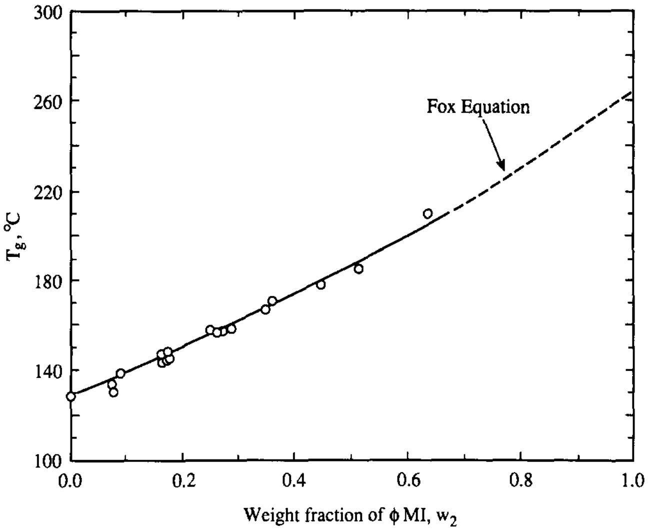

Figure 4 T_g *versus* weight fraction of comonomer ϕMI for PMMA-ϕMI copolymers. The line is drawn to the Fox equation

Plateau modulus: locus of invariant point

We first establish that the G' value at $(\tan \delta)_{\min}$ in the plateau zone is invariant with respect to molecular weight and distribution (polydispersity), and verify that G_N^0 can be determined by this method within ~10% uncertainty. This is shown for a series of PMMA in *Table 1*.

The G_N^0 values obtained at $(\tan \delta)_{\min}$ are remarkably independent of molecular weight and its distribution (polydispersity), covering ranges of $M_w \approx 80\,000$–$3\,000\,000$ and $M_w/M_n \approx 1.1$–3.9. The average value of G_N^0 is $(4.25 \pm 0.19) \times 10^6$ dyn cm^{-2} for all the PMMA samples in *Table 1*. This average value has a standard deviation of only 4.5%, and is in good agreement with those obtained by integration of loss modulus (G'') in the terminal zone (i.e. 4.3×10^6 dyn cm^{-2}). This integration requires that the G'' master curve has a maximum in the plateau zone[13]. Only the two narrow distribution samples in the present series have such a maximum, and so their G_N^0 values can be found by the integration method. Furthermore, the G_N^0 values found by the present method agree well with the literature values[4,14,15].

We have shown previously that the G_N^0 value varies with tacticity[4]. The present PMMA samples have nearly the same tacticity. Therefore, any variations of G_N^0 with tacticity in the present PMMA samples are quite small, and so may be neglected, as can be seen in *Table 1*. We will discuss the effect of tacticity on G_N^0 in PMMA in more detail elsewhere.

Two PMMA samples contain small amounts of comonomers (1% of vinyl acetate and 3.5% of methyl acrylate, respectively). These comonomers significantly improve the thermal stability, but tend to affect the G_N^0 value. The effect of comonomers on G_N^0 can be estimated by using the geometric-mean relationship between G_N^0 and composition, as shown below. Since the amounts of comonomers are small, we showed that they have negligible effects on the G_N^0 of the two samples.

Plateau modulus: compositional dependence

The G_N^0 *versus* volume fraction v_2 is plotted linearly for PMMA-S and PMMA-ϕMI in *Figure 5*. It can be seen that the G_N^0 *versus* v_2 curves deviate negatively from linear additivity for both copolymers. The negative deviation is especially pronounced in PMMA-ϕMI. Negative deviations were also found in PMMA-S and poly(styrene-*stat*-acrylonitrile) by Lomellini and Rossi[16].

The G_N^0 value for the homopolymer of ϕMI could not be measured, since samples with sufficiently high molecular weights suitable for such measurement could not be prepared. Therefore, its value (shown as a triangle symbol) is estimated independently by a group contribution method, discussed later.

Figure 6 shows that log G_N^0 *versus* v_2 gives a straight line for both PMMA-S and PMMA-ϕMI, respectively. This means that the G_N^0 of a copolymer is the geometric mean of those for the homopolymers, i.e.

$$\log G_N^0 = v_1 \log G_{N_1}^0 + v_2 \log G_{N_2}^0 \qquad (5)$$

where $G_{N_j}^0$ is the plateau modulus for the homopolymer of comonomer j and v_j the volume fraction of comonomer j.

All the measured G_N^0 values (dyn cm^{-2}) are fitted to equation (5) by least-squares to obtain

$$\log G_N^0 = v_1 \log(4.26 \times 10^6) + v_2 \log(1.53 \times 10^6) \qquad (6)$$

for PMMA-S copolymers, and on the other hand,

$$\log G_N^0 = v_1 \log(4.26 \times 10^6) + v_2 \log(1.30 \times 10^5) \qquad (7)$$

for PMMA-ϕMI copolymers. The above two equations are drawn as solid straight lines in *Figures 5* and *6*.

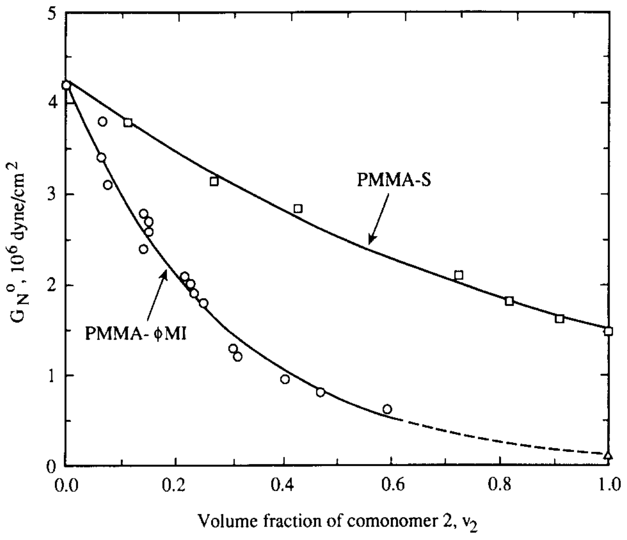

Figure 5 G_N^0 *versus* volume fraction of comonomer, v_2, for PMMA-S and PMMA-ϕMI

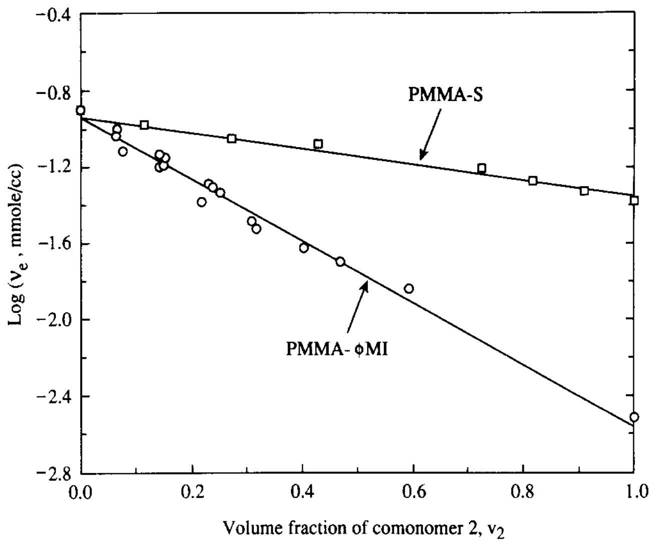

Figure 6 Semilog plots of G_N^0 *versus* volume fraction of comonomer 2, v_2, for PMMA-S and PMMA-ϕMI

It is interesting to note that the above least-squares regression of measured G_N^0 values, i.e. equation (7), predicts that the G_N^0 value for the homopolymer of ϕMI is 1.3×10^5 dyn cm^{-2}, in good agreement with the value of 1.4×10^5 dyn cm^{-2} estimated independently by the group contribution method.

Group contribution

The characteristic ratio C_∞ of a chain is defined by[4,17,18]:

$$C_\infty = \lim_{n \to \infty} \langle R_0^2 \rangle / (n \langle l_v^2 \rangle) \qquad (8)$$

where n is the number of statistical skeletal units (defined below) in a chain, $\langle R_0^2 \rangle$ the mean-square end-to-end distance of an unperturbed chain and $\langle l_v^2 \rangle$ the mean-square length of a statistical skeletal unit.

A statistical skeletal unit is a real or virtual skeletal bond, which is an elementary rotational unit determining the rotational conformation of the chain[4,17,18]. Factors which should be considered in determining a statistical skeletal bond include bond rotational states, coplanarity and tautomerism of the skeletal units. For instance, a single bond (such as C–C) can rotate around its own bond axis, and so is a statistical real bond. On the other hand, the C–C bonds in an aromatic ring cannot rotate around their own axes. Therefore, a *p*-phenylene group with the two connecting single bonds (i.e. –ϕ–) is an elementary rotational unit, and so is a statistical virtual bond.

Figure 7 shows the minimum energy conformation for a trimer of ϕMI. There are two skeletal virtual bonds in the trimer: one consisting of carbon atoms 2–4, and the other consisting of carbon atoms 4–6. The average spatial length of such a virtual bond is 2.51 Å (*Table 5*).

The intrinsic viscosity ($[\eta_\theta]$) in θ conditions is given by[17,19]:

$$[\eta_\theta] = K_\theta M^{1/2} = \phi_0 \langle R_0^2 \rangle^{3/2} / M \qquad (9)$$

where K_θ is the Flory intrinsic viscosity constant, $\phi_0 = 2.51 \times 10^{23}$ cm^3 mol$^{1/2}$ g$^{-3/2}$, and M the molecular weight.

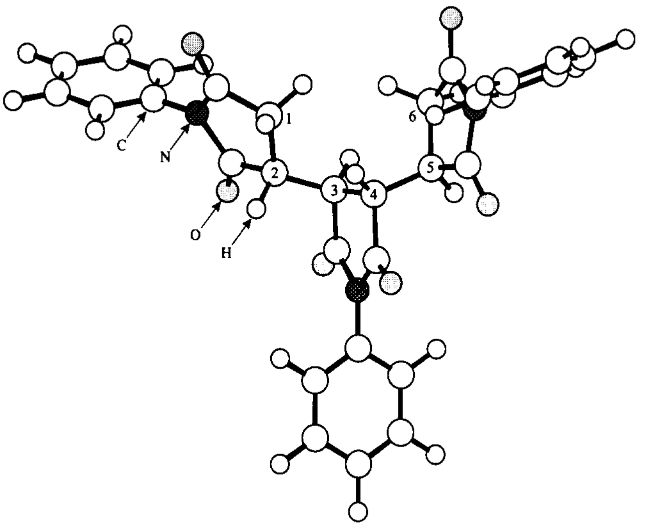

Figure 7 Minimum energy conformation for the trimer of ϕMI, showing two skeletal virtual bonds, i.e. the unit consisting of carbon atoms from 2 to 4, and that from 4 to 6

Combining equations (8) and (9), we have[4]:

$$C_\infty = (K_\theta/\phi_0)^{2/3} M_r/(n_v \langle l_v^2 \rangle) \qquad (10)$$

where M_r is the average molecular weight of a repeat unit, and n_v is the number of statistical skeletal units (real and virtual bonds) per repeat unit. Relevant n_v and $\langle l_v^2 \rangle$ values are listed in *Table 5*.

Moreover, we have previously shown that N_v the number of statistical skeletal units in an entanglement strand (i.e. between two consecutive entanglement junctions) is given by[4]:

$$N_v = 3C_\infty^2 \qquad (11)$$

Combining equations (3) and (11), we have

$$C_\infty = [\rho RT/(3G_N^0 M_v)]^{1/2} \qquad (12)$$

where $M_v = M_r/n_v$ is the average molecular weight per statistical skeletal unit. Combining equations (10) and (12), we have

$$G_N^0 = [\rho RT/(3M_v)](\phi_0/K_\theta)^{4/3}(\langle l_v^2 \rangle/M_v)^2 \qquad (13)$$

which relates G_N^0 to the K_θ of the intrinsic viscosity equation for unperturbed chains.

The K_θ is related to L_r the molar stiffness function of a repeat unit by[11]:

$$K_\theta = (L_r/M_r)^2 \qquad (14)$$

The molar stiffness function L_r is a group additive function, given by[11]:

$$L_r = \sum K_i + 4.2n_r \qquad (15)$$

where K_i is the molar stiffness constant of group i and n_r the number of real skeletal bonds (not statistical skeletal units) in a repeat unit. Therefore, G_N^0 can be predicted from chemical structure by group contribution, if the molar stiffness constants for the groups are known.

Table 6 lists relevant K_i group constants for the present systems. All values are taken from van Krevelen[11], except for ϕMI whose value was unavailable before and so is determined here.

We relate the measured G_N^0 to K_i by using equations (14) and (15) in equation (13). We can thus calculate the K_i value for the ϕMI group from the G_N^0 value for each of the PMMA-ϕMI copolymers. The results are plotted in *Figure 8*.

If our proposed equations and method are correct, the $K_i(\phi\text{MI})$ value thus obtained should be independent of the composition of the copolymer. This is indeed true, as shown in *Figure 8*. The $K_i(\phi\text{MI})$ values appear to fluctuate randomly. The fluctuation is larger in the range where the copolymers have small amounts of ϕMI comonomer, because the $K_i(\phi\text{MI})$ value is the difference of two numbers of comparable magnitude in this range. As the amount of ϕMI comonomer increases, the fluctuation becomes smaller, giving an average value of

$$K_i(\phi\text{MI}) = 75.2 \pm 10.5\ \text{g}^{1/4}\,\text{cm}^{3/2}\,\text{mol}^{-3/4} \qquad (16)$$

This K_i value for ϕMI is listed in *Table 6*.

We can now calculate the G_N^0 value for the homopolymer of ϕMI by using the above value in equation (15) to obtain the value for L_r. Then, using equation (14) in equation (13), we obtain

$$G_N^0 = (1.4 \pm 0.3) \times 10^5\ \text{dyn cm}^{-2} \qquad (17)$$

for the homopolymer of ϕMI. (This value is plotted as a triangle in *Figures 5* and *6*.)

We have thus estimated the G_N^0 value for the homopolymer of ϕMI by two independent methods. The first is by the extrapolation of experimental data of PMMA-ϕMI copolymers according to the geometric-mean equation, i.e. equations (5) or (6), obtaining $G_N^0 = 1.3 \times 10^5$ dyn cm^{-2}. The second is by the group contribution method, using equation (13), obtaining $G_N^0 = 1.4 \times 10^5$ dyn cm^{-2}. These two independently estimated values are in good agreement with each other. This supports the validity of our proposed equations and method.

The group contribution method has been shown to be applicable for predicting the G_N^0 and M_e of wide varieties of chain structures, discussed elsewhere[20].

Entanglement molecular weight

The M_e and the entanglement density (ν_e) are directly related to the density and G_N^0 by equation (3). Since the melt density varies smoothly with composition, we thus expect that M_e and ν_e should also follow the geometric-mean relationship, just like G_N^0. This is indeed found to be true, as shown in *Figures 9* and *10*.

Least-squares regression gives the following results for M_e (in g mol^{-1}) and ν_e (in mmol cm^{-3} at 95°C). For

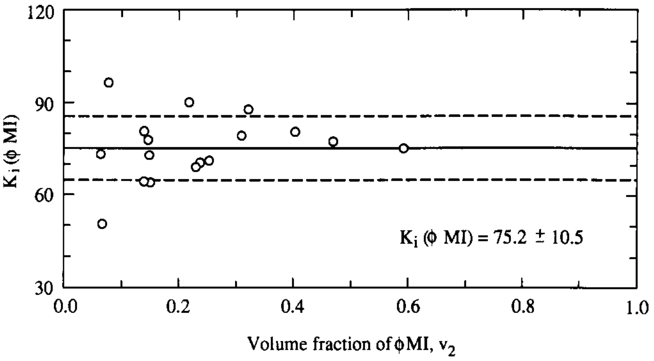

Figure 8 Molar group constant K_i for ϕMI *versus* copolymer composition (i.e. volume fraction of comonomer ϕMI) calculated from G_N^0 data of PMMA-ϕMI

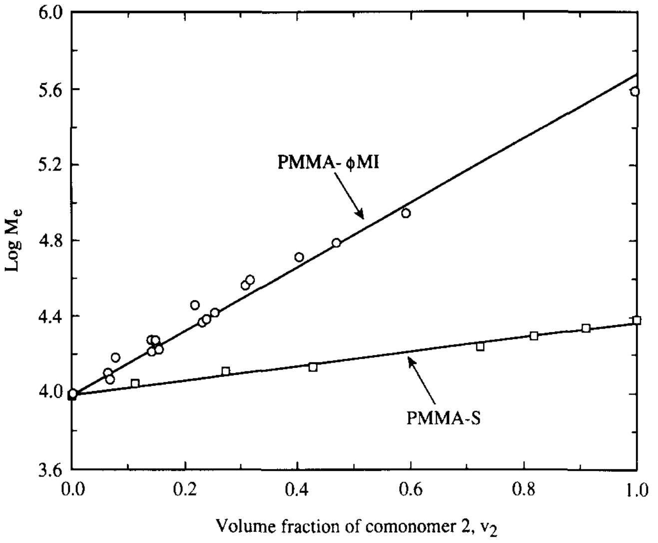

Figure 9 Semilog plots of M_e (g mol^{-1}) *versus* volume fraction of comonomer 2, v_2, for PMMA-S and PMMA-ϕMI

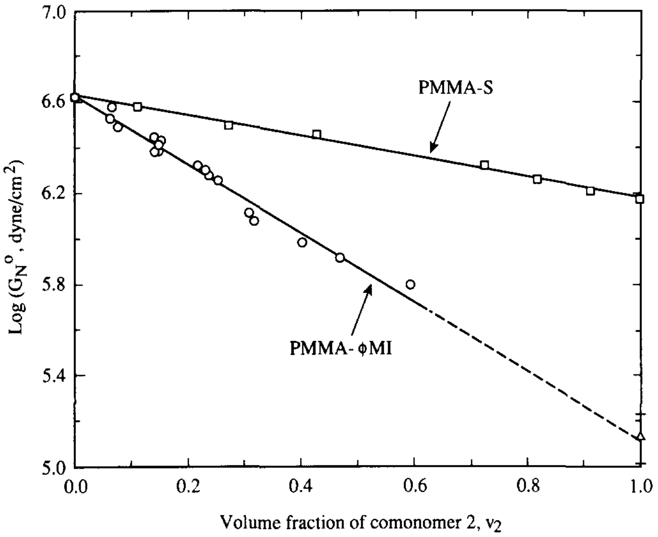

Figure 10 Semilog plots of ν_e (in mmol cm^{-3} at 95°C) *versus* volume fraction of comonomer 2, v_2, for PMMA-S and PMMA-ϕMI

PMMA-S copolymers, we have

$$\log M_e = 3.989 v_1 + (4.377 \pm 0.010) v_2 \qquad (18)$$

$$\log \nu_e = -0.934 v_1 - (1.350 \pm 0.012) v_2 \qquad (19)$$

For PMMA-ϕMI copolymers, we have

$$\log M_e = 3.989 v_1 + (5.678 \pm 0.035) v_2 \qquad (20)$$

and

$$\log \nu_e = -0.934 v_1 - (2.539 \pm 0.033) v_2 \qquad (21)$$

Figures 9 and *10* plot M_e and ν_e (mmol cm^{-3} at 95°C) *versus* composition for PMMA-S and PMMA-ϕMI copolymers, respectively.

Terpolymers

It is interesting to note that any polymer may be considered to be a copolymer of its constituent structural units. For instance, a terpolymer such as PMMA-S-ϕMI may be regarded as a copolymer of MMA-S and ϕMI or MMA and S-ϕMI or MMA-ϕMI and S. Furthermore, a homopolymer such as PMMA may be regarded as an alternating copolymer of $-CH_2-$ and $-C(CH_3)(O{=}C{-}OCH_3)-$. Therefore, any law valid for copolymers must also be valid for any homopolymers and multicomponent copolymers. It can be shown readily that the geometric-mean law, i.e. equation (5), indeed meets this mathematical requirement.

Therefore, for terpolymers, we have

$$\log G_N^0 = v_1 \log G_{N_1}^0 + v_2 \log G_{N_2}^0 + v_3 \log G_{N_3}^0 \qquad (22)$$

The G_N^0 values for several PMMA-S-ϕMI terpolymers are thus predicted from those of the homopolymers by equation (22). In the calculations, the G_N^0 values used for the homopolymers are 4.2×10^6 dyn cm^{-2} for PMMA, 1.5×10^6 dyn cm^{-2} for PS and 1.4×10^5 dyn cm^{-2} for PϕMI. The predicted G_N^0 values for the terpolymers are in good agreement with the measured values (*Table 4*).

CONCLUSIONS

The plateau modulus G_N^0 is shown to equal G' at the minimum of $\tan\delta$ in the plateau zone. The plateau modulus G_N^0 and the M_e of statistical copolymers follow the geometric-mean relationship with respect to composition, i.e. $\log G_N^0 = \sum v_j \log G_{N_j}^0$ and $\log M_e = \sum v_j \log M_j$, where v_j is the volume fraction of comonomer j. We have also illustrated how the G_N^0 and M_e of homopolymers and copolymers can be estimated from chemical structure by group contribution.

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