BUTTERWORTH
HEINEMANN

Polymer Vol. 36 No. 8, pp. 1627-1633, 1995

0032-3861/95/$10.00+0.00

On the role of entanglements in the embrittlement of poly(methyl methacrylate) based random copolymers

P. Tordjeman*, J. L. Halary† and L. Monnerie
Laboratoire de Physicochimie Structurale et Macromoléculaire, Ecole Supérieure de Physique et Chimie Industrielles de la Ville de Paris, 10 rue Vauquelin, 75231 Paris Cedex 05, France

and A. M. Donald
Cavendish Laboratory, University of Cambridge, Madingley Road, Cambridge CB3 0HE, UK
(Received 25 April 1994)

Composition dependences of the glass transition temperature (T_g), the molecular weight between entanglements (M_e) and the thin film deformation behaviour have been studied in two series of methyl methacrylate-based random copolymers. When the comonomer is styrene, increases in both M_e and brittle behaviour accompany the decrease of T_g. When the comonomer is *N*-substituted maleimide, the same conclusions hold with increasing T_g. For both series of materials, a correlation is proposed between the number of skeletal bonds in an entanglement strand, N_e, and the quantity ($T_g - T_{cs}$), where T_{cs} is the lower temperature at which shear deformation is observed in thin films in competition with crazing.

(Keywords: poly(methyl methacrylate); copolymers; brittleness)

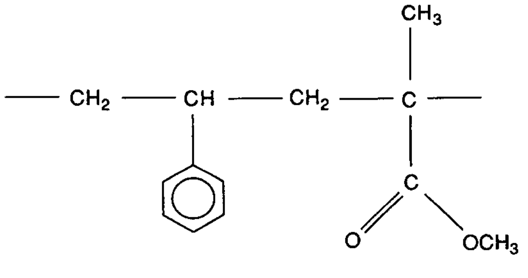
INTRODUCTION

Polystyrene (PS) and many other amorphous glassy polymers suffer from brittle behaviour, even at temperatures approaching their glass transition temperature, T_g. In contrast, poly(methyl methacrylate) (PMMA) is known to have some ductility at temperatures well below its T_g. It is also known from analysis of polymer deformation mechanisms that brittleness is associated with craze occurrence, whereas ductility results from the presence of shear deformation zones. As demonstrated by Kramer, Donald and co-workers[1-5], two molecular processes are responsible for crazing, depending on temperature T. Low temperature crazing can occur only by a loss of strands in the entanglement network as the result of chain scission, the rate of which is independent of polymer molecular weight. In contrast, chain disentanglement becomes an important mechanism in high temperature crazing. This conclusion is supported by the fact that the rate of the crazing processes becomes a strongly decreasing function of molecular weight when T approaches T_g.

In the case of PS, it has also been shown that this polymer exhibits a transition from brittle to ductile, i.e. from crazing to shear deformation, as the deformation temperature is increased. Furthermore, the temperature at which this transition occurs decreases with increasing molecular weight. This observation has been interpreted as being the result of chain disentanglement to form fibril surfaces[6].

All the basic concepts dealing with the role of entanglements in the deformation of amorphous glassy polymers have been summarized in a very recent publication[7].

The object of the current work was to investigate the progressive embrittlement in PMMA by inserting at random increasing amounts of comonomer units. In what follows we focus on two series of amorphous random copolymers. The first series, called SM, consists of styrene–methyl methacrylate materials (**I**) with styrene content in the range 0–100 mol%. The second, called MIM, deals with *N*-substituted maleimide–methyl methacrylate materials (**II**), with various substituents (cyclohexyl, phenyl, isopropyl) and maleimide content in the range 0–25 mol%.

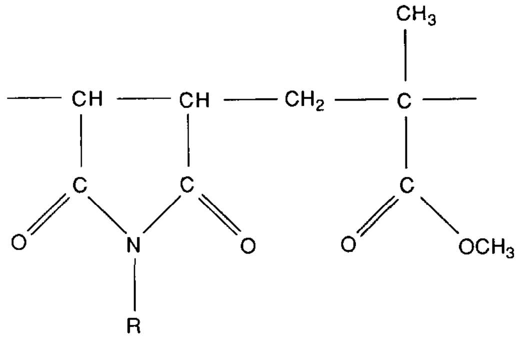


I

---

* Present address: Elf Atochem, Groupement de Recherches de Lacq, 64170 Artix, France

† To whom correspondence should be addressed



II

Analysis of the competitive deformation processes is based on Lauterwasser and Kramer's copper-grid technique[8]. In this technique, thin films are bonded to copper grids and strained in tension under an optical microscope to produce deformation instabilities which are then characterized by transmission electron microscopy either as crazes or shear deformation zones.

Viscoelastic measurements were also performed on the copolymers under study to determine their glass transition temperatures and to derive the number of skeletal bonds in an entanglement strand. The corresponding results are given in this paper in an attempt to correlate the brittle-to-ductile transition of these materials with polymer properties on the molecular scale.

EXPERIMENTAL

Materials

PMMA, PS and the SM copolymers were obtained, some years ago, from Orkem. Their chain characteristics, including molecular weights, polydispersity and tacticity, have already been determined and published[9].

The MIM series of copolymers were specially synthesized for us by P. Gaillard and S. Nowé, of Elf Atochem (Lacq Research Center).

Prior to their analysis, all samples except PS were purified by precipitation with methanol from a chloroform solution. This operation allowed removal of the low molecular weight chains (typically, $\bar{M}_w \leqslant 5000\,\mathrm{g\,mol^{-1}}$) and measurement of polydispersities in the range 1.8–2.2. Sample characteristics are summarized in *Table 1*. The overall content and random distribution of the *N*-substituted maleimide units were checked by ^{1}H n.m.r. It was also verified that the presence of maleimide units does not affect the tacticity of the MMA-based copolymers: the ratio $S/S+H$ (where S and H are the percentages of syndiotactic and heterotactic diads, respectively) remained equal to 0.61 ± 0.02 regardless of the material under study.

Viscoelastic measurements

The glass transition region was explored using an MTS 831-10 hydraulic testing machine operated in the tensile mode. Bars with dimensions of $60 \times 12 \times 3\,\mathrm{mm}^3$ were subjected to a static strain of 0.1% on which was superimposed a sinusoidal strain varying from -0.05 to 0.05%. The temperature increment between successive measurements was 2°C. Data reported here were obtained at a frequency of 1 Hz. The glass transition temperature, T_g, is conventionally defined as the temperature at which the loss modulus, E'', passes through a maximum. At the same temperature, the storage modulus, E', exhibits an inflection point. As previously reported[9], this temperature is the same, within experimental error, as the T_g defined at the onset of differential scanning calorimetry traces.

The rubbery plateau and terminal zones were investigated by oscillatory shear experiments performed on a Rheometrics RMS 605. Measurements were carried out in the laboratory of Professor R. Muller, at the Institute Charles Sadron of Strasbourg. Discs 25 mm in diameter and 1.6 mm thick were subjected to a strain varying from 1% in the plateau region to 7% in the terminal zone at driving frequencies covering the range 0.01–$100\,\mathrm{rad\,s^{-1}}$. The pseudo-equilibrium modulus of the entanglement network, G_N^0, was taken, as usual[10], as the value of the storage modulus G' at the frequency where $\tan\delta = G''/G'$ is at its minimum in the plateau region. The average molecular weight between coupling loci, M_e, was derived

Table 1 Characteristics of the MMA-based materials

Polymer code	Nature of comonomer	Comonomer content (mol %)	$\bar{M}_n$ ($\mathrm{g\,mol^{-1}}$)	$\bar{M}_w$ ($\mathrm{g\,mol^{-1}}$)	Polydispersity index
PMMA	none	0	66000	118500	1.8
SM25	styrene	25.0	62500	137000	2.2
SM50	styrene	50.0	69000	139000	2.0
SM75	styrene	75.0	98500	193000	2.0
PS	pure styrene	100	150000	265000	1.8
CMIM5	*N*-cyclohexylmaleimide	5.0	65000	118500	1.8
CMIM7	*N*-cyclohexylmaleimide	6.7	63000	116000	1.8
CMIM8	*N*-cyclohexylmaleimide	8.0	71500	143500	2.1
CMIM10	*N*-cyclohexylmaleimide	10.0	69000	126000	1.8
CMIM15	*N*-cyclohexylmaleimide	15.0	73500	151500	2.1
CMIM20	*N*-cyclohexylmaleimide	20.0	67500	134000	2.0
CMIM25	*N*-cyclohexylmaleimide	25.0	71000	156000	2.2
IMIM15	*N*-isopropylmaleimide	15.0	64000	116500	1.8
PMIM15	*N*-phenylmaleimide	15.0	53500	113000	2.1

Table 2 Glass transition temperature of the MMA-based random copolymers

Polymer code	T_g(°C)
PMMA	126
SM25	115[a]
SM50	107[a]
SM75	106.5[a]
PS	105.5[a]
CMIM5	132.5
CMIM7	133.5
CMIM8	135
CMIM10	139
CMIM15	145.5
CMIM20	153
CMIM25	161.5
IMIM15	133
PMIM15	149

[a] Data taken from ref. 9

from G_N° through the relation[10]:

$$M_e = \frac{\rho RT}{G_N^\circ}$$

where ρ is the volumic mass and R the gas constant. The front factor g_N has been omitted in this equation, because it is arbitrarily supposed to be equal to unity. Finally, the number of real skeletal bonds in an entanglement strand, N_e, was extracted from M_e according to Wu's relationship[11]:

$$N_e = \frac{2M_e}{M_r}$$

In this equation, the factor of 2 represents the number of skeletal bonds in any repeat unit and M_r was taken as the mole fraction average of the molecular weights of the two types of repeat units.

All samples used in viscoelastic measurements were compression moulded under vacuum, at a temperature around $T_g + 60$°C. Samples were stored in a vacuum oven at 60°C before use in order to eliminate any moisture which might be associated with the carbonyl groups.

Procedure of the copper-grid technique

Uniform thin films were produced by drawing dust-free glass slides at a constant rate of $1\,\mathrm{mm\,s^{-1}}$ from 4 wt% solutions of copolymer in chloroform. In all cases, the film thickness was held constant at $0.5\,\mu$m. After solvent evaporation, the film was floated off on the surface of a water bath and then picked up on a well-annealed copper grid. Finally, the film was bonded to the grid by drying under vacuum at 60°C for 36 h. It was verified that no constraints or crazes were present in the sample at this stage.

The grids were then mounted in a home-made strain frame and strained in tension at a constant strain rate of $2 \times 10^{-3}\,\mathrm{s^{-1}}$ and at temperatures ranging from 20°C to T_g. Straining continued until the first deformation instability was detected through the reflection optical microscope attached to the equipment. Finally, the grids were removed for examination by transmission electron microscopy (Jeol 200 EX at 200 keV), in order to determine the nature of the instabilities – crazes or shear deformation zones – which had occurred.

RESULTS AND DISCUSSION

First, let us consider the glass transition temperatures of the materials (*Table 2*). As recalled in *Figure 1*, it has been shown previously[9] that the progressive replacement of MMA units by styrene in the SM series of copolymers leads to a decrease of T_g (1 Hz). However, the composition dependence is non-linear: a small fraction of styrene units affects the glass transition of the copolymers much more than a small fraction of MMA units. This behaviour was explained by emphasizing the role of the intrachain and interchain polar interactions between the ester groups. In the MMA-rich copolymers, small amounts of styrene are probably sufficient to dramatically reduce these interactions as compared with pure PMMA, resulting in a drop in T_g. Conversely, small amounts of MMA distributed at random in the styrene-rich copolymers are not sufficient to permit substantial polar–polar interactions, thus T_g remains close to that of pure PS.

The T_g behaviour is quite different in the case of the copolymers of the MIM series. This result is illustrated in *Figures 2* and *3* which give, respectively, the temperature dependence of the loss modulus in the T_g region for some CMIM copolymers of different composition and for different *N*-substituted MIM of same composition. Systematically, an increase in T_g (1 Hz) with increasing maleimide content is observed compared with that of pure PMMA (*Figure 1*). Regardless of the nature of the substituent on the maleimide ring, polar MMA units are progressively replaced by maleimide units which are also polar. Thus, in contrast to the SM series, the occurrence of polar interactions is no longer the dominant factor responsible for the composition dependence of T_g. Instead, the increase in T_g can be explained by the increased rigidity imposed on the main chain by the presence of the maleimide rings. The nature of the *N*-substituent on the ring is of minor importance for T_g, especially when comparing side groups of similar molar volume such as cyclohexyl and phenyl. However, the increase in T_g is noticeably less pronounced in the case of *N*-isopropylmaleimide.

Secondly, it is interesting to characterize the copolymers

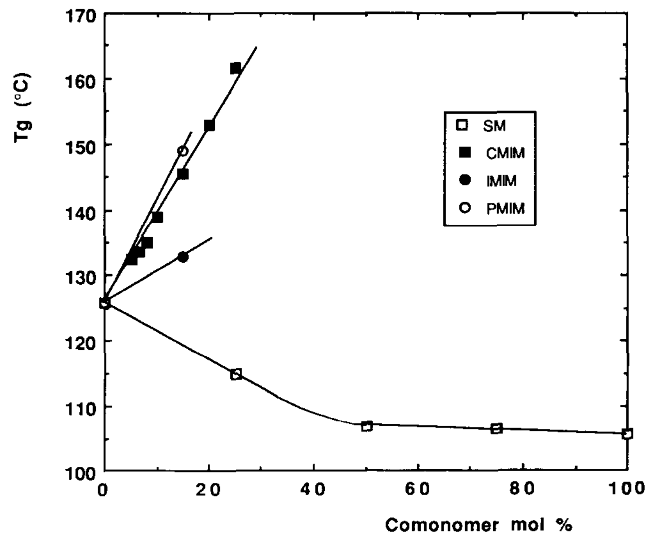


Figure 1 Influence of comonomer content on the glass transition temperature of SM and MIM copolymers

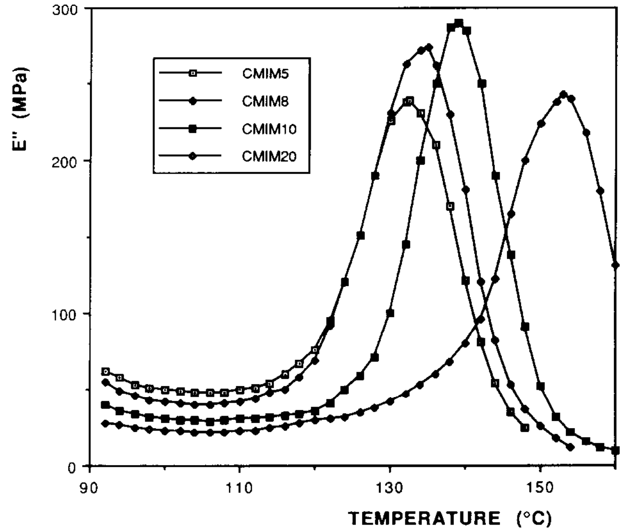


Figure 2 Temperature dependence of the loss modulus E'' of CMIM5, CMIM8, CMIM10 and CMIM20 in the glass transition region (frequency: 1 Hz)

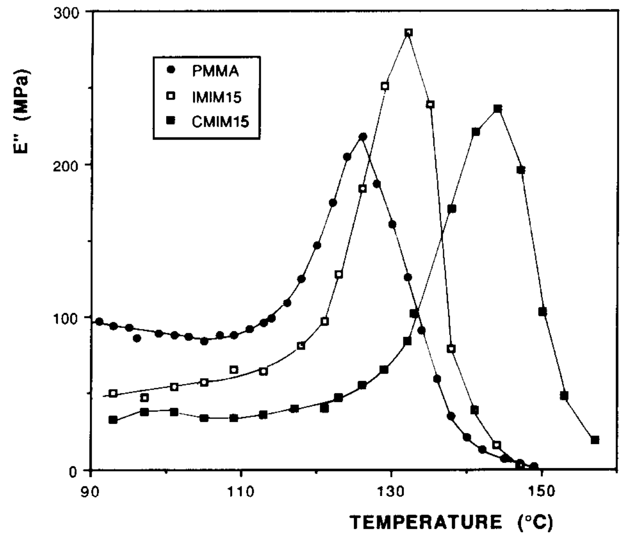


Figure 3 Temperature dependence of the loss modulus E'' of PMMA, CMIM15 and IMIM15 in the glass transition region (frequency: 1 Hz)

further by comparing their viscoelastic behaviour in the plateau region. Experimental data relative to the SM series have already been published, as detailed in ref. 9. The same approach was developed for all the materials of the MIM series. Conservative shear modulus, G', and loss shear modulus, G'', were plotted as a function of frequency at different temperatures. The corresponding master curves were then derived according to the frequency–temperature superposition principle[10]. As an example, the master curve for copolymer CMIM15, with T_g (1 Hz) taken as the reference temperature, is given in *Figure 4*. The tensile MTS data in the low temperature range fit well with the shear Rheometrics data obtained at higher temperatures, taking into account a Poisson's ratio of $\nu = 0.44$ at T_g and non-negligible changes in volumic mass at high temperature. This agreement between tensile and shear data has been previously reported in the SM series[9].

The values of the pseudo-equilibrium modulus of the entanglement network, G_N°, were taken as the values of G' at the frequency of the minimum of $\tan\delta$. They are given in *Table 3*, together with those relative to the SM series. The average molecular weight between coupling loci, M_e, and the number of real skeletal bonds in an entanglement strand, N_e, were derived from G_N°, following the calculation procedure detailed in the Experimental section. Values of M_e and N_e are also reported in *Table 3*.

The sensitivity of N_e to the comonomer content is illustrated in *Figure 5*. Compared with pure PMMA, it is clear that the presence of both styrene units and maleimide units leads to a systematic increase in the

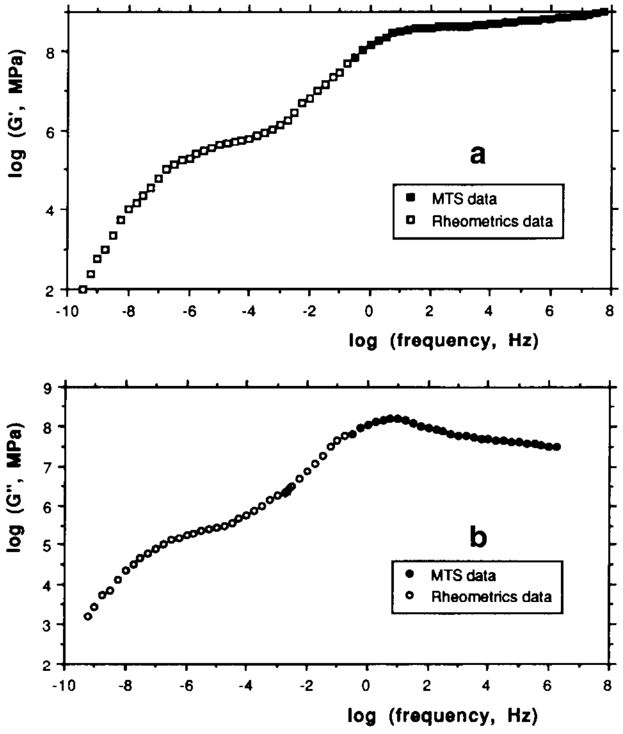


Figure 4 Master curves of copolymer CMIM15 at 145°C: (a) storage modulus from MTS and Rheometrics measurements; (b) loss modulus from MTS and Rheometrics measurements

Table 3 Entanglement characteristics of the MMA-based random copolymers

Polymer code	G_N° (MPa)	M_e (g mol^{-1})	N_e	C_∞ (estimated)
PMMA	0.66^a; 0.74^b	6 000	120	6.5
SM25	0.46^a	$8\,200^c$	162^c	7.5_5
SM50	0.33^a	$11\,500^c$	226^c	8.9
SM75	0.29^a	$16\,600^c$	322^c	10.6
PS	0.20^a	$18\,000^c$	346^c	11.0
CMIM5	$0.44_5{}^b$	10 000	191	8.2
CMIM7	0.40^b	11 200	211	8.6
CMIM8	0.38^b	11 800	224	8.8_5
CMIM10	$0.34_5{}^b$	13 000	241	9.2
CMIM15	$0.22_5{}^b$	20 100	359	11.2
CMIM20	0.16^b	27 700	478	12.9
CMIM25	0.11^b	40 000	668	15.2_5
IMIM15	0.29^b	15 500	292	10.1
PMIM15	$0.23_5{}^b$	19 000	342	10.9_5

[a] At a reference temperature of 140°C
[b] At a reference temperature of 200°C
[c] Data taken from ref. 9

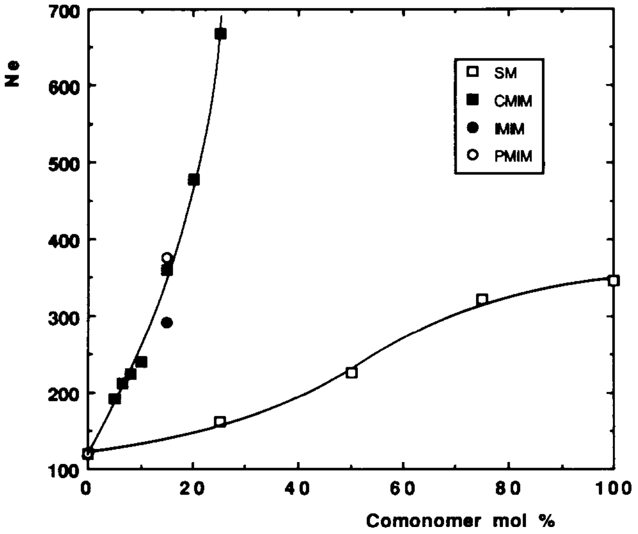


Figure 5 Influence of comonomer content on the number of skeletal bonds in an entanglement strand, N_e, for SM and MIM copolymers

number of bonds between entanglements. This increase with increasing comonomer content follows an S-shaped curve in the SM series[9]. No conclusion on the profile can be inferred in the MIM series because the composition range under study is too restricted. A crucial feature of the MIM series is the strong increase in N_e with increasing maleimide content; as an example, 15 mol% of maleimide units produce the same effect on N_e as 75 mol% of styrene units. Obviously, the rigidity of the maleimide moieties can be thought to be responsible for this behaviour. Thus, it is not surprising to observe that, within experimental error, the nature of the *N*-substituent has no effect on the values of N_e.

Furthermore, the values of N_e may be used to produce a rough estimate of Flory's[12] characteristic ratio

$$C_\infty = \langle r^2 \rangle / nl^2$$

which accounts for the end-to-end distance of the macromolecular chains. The calculation which follows is based on the approach of Wu, who showed that N_e is linearly related to the square of C_∞ for a large variety of polymers, including both polystyrene and poly(methyl methacrylate)[11]. Let us assume that the bulk values of C_∞ for PS and PMMA agree with their values in theta solvent, i.e. 11.0 and 6.5, respectively[13]. We can then extract the values of the coefficients α and β from the equation:

$$\log N_e = 2\alpha \log C_\infty + \beta$$

applied to both PS and PMMA. Finally, knowing N_e, α and β, C_∞ can be calculated for the copolymers. The relevant values of C_∞ are given in *Table 3*. They have to be regarded as estimates because of the large error bars attached to the method of calculation and the crucial influence of the values of C_∞ taken for PS and PMMA.

We now turn to the main purpose of this paper, which is to report on the competitive deformation processes observed in thin films by using the copper-grid technique. Some years ago, we made an attempt to separate three types of deformation mechanisms in the SM copolymers: crazing, localized shear banding and diffuse shear banding[14]. Some ambiguities accompanied the identification of localized shear bands at that time. Moreover, further study of the MIM series did not corroborate the presence of localized shear bands in the low temperature range. In this paper, we focus only on the two unambiguous processes, crazing and shear deformation (called diffuse shear banding above), although localized shear banding may have occurred in some samples.

Figure 6 shows a typical craze structure in these copolymers. It has long been established[15] that all crazes exhibit a typical midrib, which is a region of lower fibril volume fraction along the middle of the craze. Alternatively, plane stress deformation zones can develop, as illustrated in *Figure 7* for the case of pure PMMA at 53°C.

The temperature ranges in which these deformation mechanisms can be observed depend strongly on the nature of the polymer under consideration (*Table 4*). Crazing is present, in a variable abundance, at any temperature in all the materials with the exception of PMMA and CMIM5. This is indicative of their high brittleness. In contrast, PMMA and CMIM5 do not readily craze at high temperature and are characterized by the unique presence of shear deformation zones. This tendency not to craze does imply that these materials are more ductile at higher temperatures. As a general rule, each polymer can be characterized by a temperature, T_{cs}, at which crazes continue to appear but with shear deformation zones beginning to develop at the tips of the crazes, at an angle of about 45° towards the strain axis. Exceptions to this are PS and CMIM25 for which shear deformation zones seem to be observed only at T_g.

We propose to use T_{cs} (or more realistically, $T_{cs} \pm 5°\text{C}$ due to the large error bars on this quantity) as a ductility

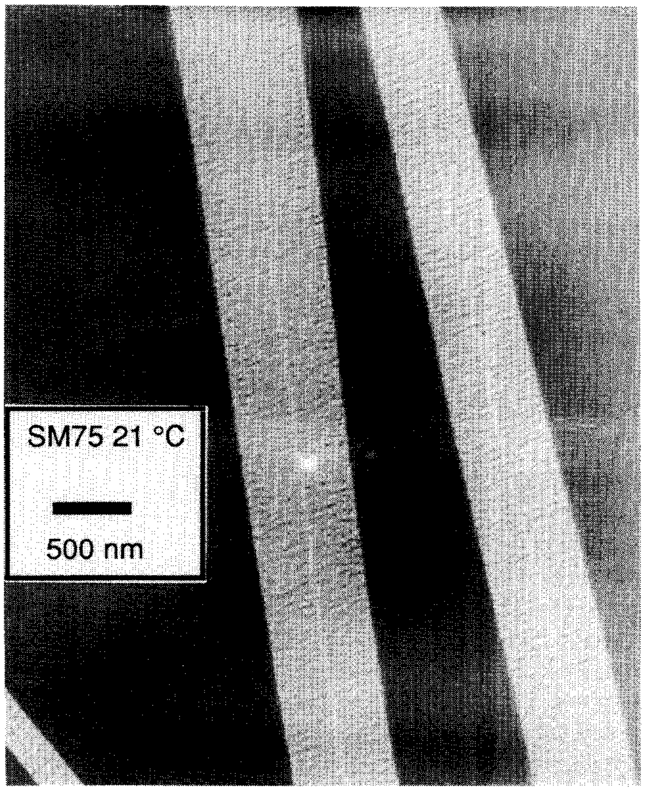


Figure 6 Typical example of craze structure. Thin film of copolymer SM75 at 21°C, strain rate: $2 \times 10^{-3}\,\text{s}^{-1}$

criterion for these materials. The higher T_{cs}, the more brittle (on an arbitrary scale) the polymer would be at a given temperature. It is worth noting that this simple criterion does not take into account the relative abundances of the two deformation processes in the specimens, which are difficult to quantify. However, an intrinsic comparison of the fracture behaviour of the materials needs to account for differences in T_g, thus we consider $(T_g - T_{cs})$ rather than simply T_{cs}. The greater $(T_g - T_{cs})$, the more ductile the polymer. It is apparent from *Table 4* that progressive substitution of styrene or maleimide units to the methyl methacrylate units leads to an increased embrittlement of the copolymers.

From a qualitative viewpoint, the value of the quantity $(T_g - T_{cs})$ seems to be related to the number of real skeletal bonds in an entanglement strand N_e(*Figure 8*). In the SM series, $(T_g - T_{cs})$ decreases sharply when N_e increases. The same kind of dependence of $(T_g - T_{cs})$ on N_e is also observed, although weaker and more scattered, in the MIM series of copolymers. The error bars on both N_e and $(T_g - T_{cs})$ are perhaps greater than anticipated in *Figure 8*. Therefore, this figure might be re-read as a unique curve of decline of $(T_g - T_{cs})$ as a function of N_e irrespective of the chemical nature of the comonomer. Inspection of the fracture characteristics of other methyl methacrylate-based random copolymers will answer this question. This work is currently in progress in our laboratory. The important conclusion at this stage of the study is that brittleness in the materials increases as the molecular weight between entanglements is increased. This result is in agreement with the earlier findings of Donald and Kramer[6].

Crude arguments may be invoked to justify this correlation between brittle behaviour and entanglements. T_{cs} can be considered as being the temperature at which the critical stress for shear instability formation, σ_s, is sufficiently low to match the critical stress for craze

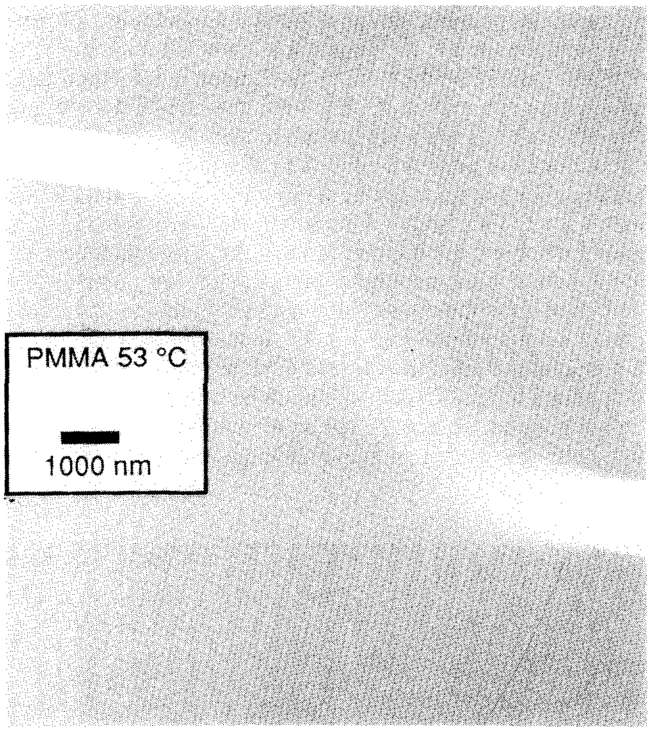


Figure 7 Typical example of shear deformation zone. Thin film of PMMA at 53°C, strain rate: $2 \times 10^{-3} s^{-1}$

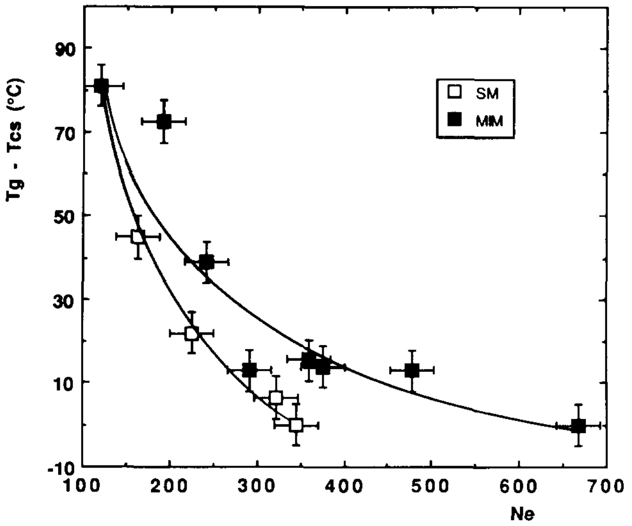


Figure 8 Correlation between $(T_g - T_{cs})$ and N_e for the entire set of materials under study

Table 4 Temperature dependence of the deformation mechanisms in thin films of MMA-based random copolymers

Polymer code	Investigated temperature range (°C)	Crazing temperature range (°C)	Shear deformation temperature range (°C)	T_{cs} (°C)	$T_g - T_{cs}$ (°C)
PMMA	20–126	20–110	45–126	45	80
SM25	20–115	20–115	70–115	70	45
SM50	20–107	20–107	85–107	85	22
SM75	20–106.5	20–106.5	100–106.5	100	6.5
PS	20–105.5	20–105.5	–	105.5	0
CMIM5	20–132.5	20–120	60–132.5	60	72.5
CMIM10	20–139	20–139	100–139	100	39
CMIM15	20–145.5	20–145.5	130–145.5	130	15.5
CMIM20	20–153	20–153	140–153	140	13
CMIM25	20–161.5	20–161.5	–	161.5	0
IMIM15	20–133	20–133	120–133	120	13
PMIM15	20–149	20–149	135–149	135	14

growth, σ_c. According to the views of Berger and Kramer[3], σ_c should diminish dramatically when N_e is increased, as far as crazing is concerned in this temperature region. At the same time, σ_s should remain roughly the same order of magnitude for all the materials considered at a given distance from T_g. Thus, the higher N_e, the closer to T_g the temperature at which $\sigma_c = \sigma_s$ and the smaller the quantity $(T_g - T_{cs})$. Refined arguments, based on the inspection of the plastic behaviour of these copolymers, are the subject of a forthcoming publication[16].

CONCLUSION

Inspection of thin film deformation mechanisms of copolymers of methyl methacrylate with styrene and *N*-substituted maleimides leads to the conclusion that the brittle behaviour of these materials is related to the increase in molecular weight between entanglements and, thus, is irrespective of the decrease or increase of T_g with the addition of comonomer.

This finding is of practical importance in the case of the MIM copolymers, which have been designed with the aim of improving the thermomechanical properties of PMMA materials by increasing their T_g. It is shown here that this result is actually obtained at the expense of the ductile behaviour. All these materials exhibit a marked embrittlement, as compared with pure PMMA.

ACKNOWLEDGEMENTS

This research was supported by Atochem France. We gratefully acknowledge the PhD grant given to one of us (P.T.) and we especially wish to thank Patrice Gaillard and Stéphane Nowé, from GRL, for supplying the MIM copolymers, and Andy More and Ann Dray for the help in the copper-grid experiments.

REFERENCES

1 Kramer, E. J. in 'Advances in Polymer Science No. 52/53' (Ed. H. H. Kausch), Springer Verlag, Berlin, 1983

2 Donald, A. M. *J. Mater. Sci.* 1985, **20**, 2630

3 Berger, L. L. and Kramer, E. J. *Macromolecules* 1987, **20**, 1980

4 Kramer, E. J. and Berger, L. L. in 'Advances in Polymer Science No. 91/92' (Ed. H. H. Kausch), Springer Verlag, Berlin, 1990

5 Plummer, C. J. G. and Donald, A. M. *Polymer* 1991, **32**, 409

6 Donald, A. M. and Kramer, E. J. *J. Polym. Sci., Polym. Phys. Edn* 1982, **20**, 899

7 Plummer, C. J. G., Cudré-Mauroux, N. and Kausch, H. H. *Polym. Eng. Sci.* 1994, **34**, 318

8 Lauterwasser, B. D. and Kramer, E. J. *Phil. Mag.* 1979, **A-39**, 469

9 Halary, J. L., Oultache, A. K., Louyot, J. F., Jasse, B., Sarraf, T. and Muller, R. *J. Polym. Sci., Polym. Phys. Edn* 1991, **29**, 933

10 Ferry, J. D. in 'Viscoelastic Properties of Polymers', Wiley, New York, 1980

11 Wu, S. *J. Polym. Sci., Polym. Phys. Edn* 1989, **27**, 723

12 Flory, P. J. 'Statistical Mechanics of Chain Molecules', Interscience, New York, 1980

13 Brandrup, J. and Immergut, E. H. 'Polymer Handbook', Wiley-Interscience, New York, 1989

14 Tordjeman, P., Halary, J. L., Monnerie, L. and Donald, A. M. 'Proc. 8th Int. Conf. on Deformation, Yield and Fracture of Polymers', Cambridge, 8–11 April 1991, p. 55

15 Beahan, P., Bevis, M. and Hull, D. *Proc. R. Soc. London, Ser. A* 1975, **343**, 525

16 Tordjeman, P., Tézé, L., Halary, J. L. and Monnerie, L. *Macromolecules* in press