Polymer Vol. 37 No. 8, pp. 1323–1327, 1996

0032-3861/96/\$15.00 + 0.00

Effect of a tensile stress on the radiolytic degradation of poly(methyl methacrylate)

F. Thominette* and J. Verdu
ENSAM, 151 Boulevard de l'Hôpital, 75013 Paris, France
(Received 28 July 1994; revised 26 June 1995)

Plaques (2 mm thick) of atactic, bulk polymerized poly(methyl methacrylate) (PMMA) were exposed to γ-rays (dose rate 2.5 kGy h^{-1}, doses ranging from 5 to 10 kGy), at ambient temperature in a nitrogen atmosphere. Tensile-loaded samples (stress: 47 MPa) were exposed together with unloaded ones. The molecular weight distribution was studied before and after irradiation by size exclusion chromatography calibrated by PMMA quasi homodisperse standards. The yield of chain scission $G(S)$ was determined for six different doses and a total number of stressed/unstressed samples of 38. The results clearly reveal a small but significant effect of tensile loading on the rate of chain scission: $G(S)$ stressed/$G(S)$ unstressed ≈ 1.2. Two possible mechanisms are discussed. The first involves a primary radiolysis of skeleton C–C bonds. In this case, tensile loading would disfavour the cage recombination of radicals and, thus, increase $G(S)$. The second (and more frequent) mechanism results from a scission of the primary macroradical, a mechanism which could be stress-activated. Copyright © 1996 Elsevier Science Ltd.

(Keywords: poly(methyl methacrylate); radiolytic degradation; tensile stress)

INTRODUCTION

Study of the coupled effects of mechanical stresses and chemical degradation has resulted in a relatively large number of publications during the last 30 years, especially in the former USSR[1–4]. Most of these studies were based on the same experimental methodology, i.e. determining the time to rupture (lifetime) under static stress in the aggressive environment under study. Despite its high practical interest and relative simplicity from an experimental viewpoint, this approach constitutes probably the more difficult way to understand the phenomenon at the mechanistic level, because it needs in principle a good knowledge of the kinetic aspects of fracture. Unfortunately, in most cases, these latter are still far from being completely elucidated so that it remains difficult to go beyond the empirical level in this field.

An alternative approach is to determine the stress effects on the kinetics of chemical degradation. This does not resolve the whole problem of lifetime prediction but gives access to data more easily usable in kinetic modelling, at least in principle, if chemical kinetics are applicable. This latter condition is not so easy to satisfy in the case of ageing of polymers in the solid state. As a matter of fact, heterogeneities linked to the initial morphology or to the build-up of a shell–core structure (diffusion-controlled processes, photodegradation of light absorbing samples, etc.), complicate considerably the kinetic study of ageing and can play a key role in mechanical rupture.

Finally, another source of difficulty is the complexity of the degradation mechanism. In the case of radical chain oxidation, for instance, there are dozens of secondary reactions leading to dozens of different products but among which only few (chain scissions) are able to modify the mechanical behaviour. In this case, non-empirical kinetic modelling of chain scission appears very difficult, if not impossible, at the present state of our knowledge.

In a preliminary search of cases in which it could eventually be possible to reach valid conclusions on the stress effect on chemical degradation, it appeared to us that the radiolytic degradation of atactic poly(methyl methacrylate) (PMMA) could be a good candidate for the following reasons.

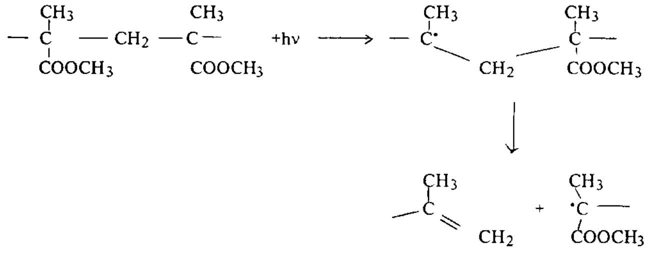
1) PMMA is completely amorphous and, in the case of γ-rays, the radiation energy is homogeneously deposited in the whole sample volume. It is noteworthy that oxygen is an inhibitor of chain scission[5], its effect is diffusion-controlled in thick samples (few mm thickness) and its diffusivity can be increased by a tensile stress, so that the presence of oxygen is to be avoided.
2) PMMA undergoes almost purely random chain scission[6].
3) The molecular weight distribution of PMMA can be determined accurately by size exclusion chromatography at ambient temperature. PMMA standards are available for the calibration.
4) PMMA is glassy at ambient temperature, its local mobility is especially low (rotations of lateral groups only), so that its modulus is relatively high (instantaneous value $E \approx 3.5$ GPa) and it can be exposed for a relatively long time under a relatively high stress without extensive creep or damage.

Difficulties in interpretation of results can arise from lack of knowledge of the degradation mechanisms despite a

---

* To whom correspondence should be addressed

relatively large number of fundamental studies[7,8]. However, the great majority of authors have reported that chain scission results from a macroradical that itself is the product radiolysis of a lateral bond, for instance:



Other variants have been proposed[9], but in all cases chain scission always results from a rearrangement (β scission) of such a macroradical.

The effect of tensile stresses on lifetime under irradiation by ionizing radiations is well established. It is generally shown that irradiation decreases the time to rupture above a certain stress level[4]. It appears very difficult to make a coherent synthesis of the proposed interpretations because they differ totally from one to another. The aim of this work is to try to establish experimentally if a tensile stress influences the rate of radiolytic chain scission in PMMA. Emphasis has been put on the statistical validity of results so that most of the important parameters, sample geometry, atmosphere (N_2), dose rate and stress value, are fixed. Our goal is simply to compare the rates of chain scission for a great number (38 pairs) of stressed and unstressed samples.

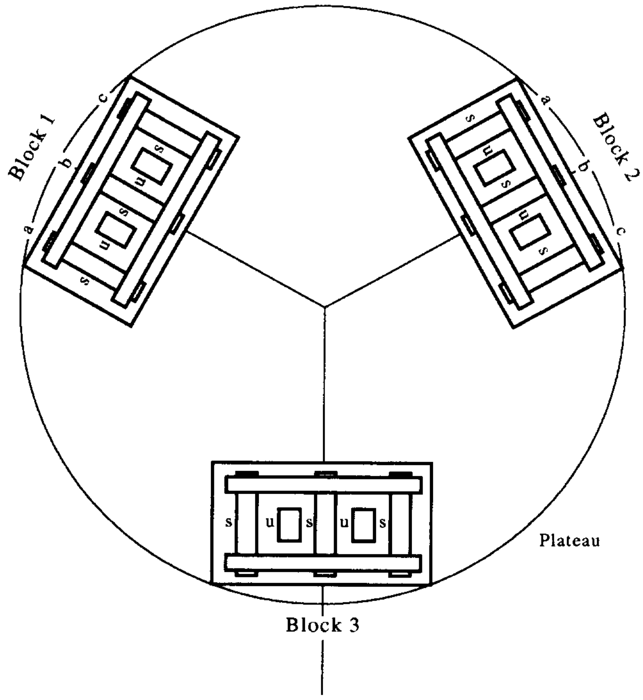


Figure 1 Schematic illustration of the sample holder. The irradiation system comprises ^{60}Co pellets disposed concentrically to the circular plateau

EXPERIMENTAL

Materials and samples

An industrial sample of bulk polymerized, atactic PMMA (Perspex plaque from ICI) was used in this study. Dogbone specimens for tensile testing, having a calibrated section of 25 × 2 mm, were machined from the original plaques of 2 mm thickness.

Irradiation

The samples were irradiated in a nitrogen atmosphere, at 25°C, by gamma rays from a ^{60}Co source, using the irradiation facilities of ORIS LABRA (CER Saclay, France). Absolute dosimetry measurements using L-alanine dosimeters were made at the sample level by the Laboratory of Metrology of Ionizing Radiations (LMRI).

The sample holder is shown schematically in *Figure 1*. It is made from three blocks placed at 120° on a circular plateau. Each block supports three stressed (s) and two unstressed (u) specimens. Various experiments, with doses ranging from about 5 to 10 kGy at a 2.5 kGy h^{-1} dose rate, were performed over a period of two years. Each experiment is characterized by: the local dose (measured on the corresponding block); the block number (1, 2 or 3); the sampling area (a, b or c) in the block; and the mechanical state (s for stressed and u for unstressed) of the sample. In most cases, two or three samples were taken in the calibrated part of the test specimen.

Loading system

The laboratory-made loading system is composed of one fixed and one mobile clamp. The displacement of the latter is monitored by the rotation of a calibrated screw, allowing a relative precision of 6.5% for the chosen amplitude of deformation (two complete rotations). A preliminary study on the tensile relaxation properties of the sample was made using an Instron 85030 dynamometer. This allowed us to determine the instantaneous and relaxation characteristics, from which it was decided to employ a constant strain amplitude of 3.6% and to start the irradiation 90 min after the onset of loading. In these conditions, the stress value, initially 76 MPa, reaches to a pseudo equilibrium value of 47 ± 5 MPa that does not undergo any significant variation during the whole exposure time.

Molecular weight determination

Molecular weight determination was made by size exclusion chromatography (s.e.c.), using tetrahydrofuran as solvent. The system was equipped with four Shodex columns, 802.5, 803, 804 and 805, and a refractometric detector. The flow rate was 1.2 ml min^{-1}.

Quasi homodisperse PMMA samples of molar weight 27, 66, 79, 265, 400, 845 and 1300 kg mol^{-1} were used for the calibration. They were supplied by Polymer Laboratories (Church Stretton, UK).

The calibration curve was a cubic, allowing a correlation coefficient of 0.9996. This calibration set is well adapted to the study of samples of weight-average molar weight typically lower than 1000 kg mol^{-1}, which is the case for all the degraded samples under study. For the virgin samples, the measured value of M_n is close to the upper standard value (1300 kg mol^{-1}) and thus carries an uncertainty. This can induce a systematic error on radiochemical yield values, but cannot affect our

Table 1 Average radiochemical yield of chain scission for stressed $[G(S)_s]$ and unstressed $[G(S)_u]$ samples

Dose (kGy)	$G(S)_s$	$G(S)_u$	$G(S)_s/G(S)_u$
5.5	2.94 ± 0.23	2.59 ± 0.22	1.13 ± 0.12
5.8	2.42 ± 0.18	2.13 ± 0.23	1.13 ± 0.15
6.1	2.94 ± 0.38	2.35 ± 0.10	1.25 ± 0.16
9.21	2.25 ± 0.56	1.75 ± 0.26	1.28 ± 0.12
9.7	1.93 ± 0.21	1.78 ± 0.13	1.08 ± 0.13
10.6	2.10 ± 0.32	1.62 ± 0.32	1.29 ± 0.08

conclusions based on the comparison of stressed and unstressed samples. Each time, s.e.c. measurements were made shortly after irradiation (a few days) and the instrument was recalibrated daily.

RESULTS

The s.e.c. measurements made on virgin samples led to: $M_{n0} = 1300\,\mathrm{kg\,mol^{-1}}$ and $M_{w0} = 3000\,\mathrm{kg\,mol^{-1}}$. Each stressed (s) sample was paired with the closest unstressed (u) one in order to minimize the eventual spatial heterogeneity of irradiation. For each pair, both samples were analysed by s.e.c. on the same day in order to avoid uncertainties due to long-term variations of the apparatus response.

The radiochemical yield of chain scission $G(S)$ was determined from the following system of equations[10]:

$$\frac{1}{M_n} = \frac{1}{M_{n0}} + \left[(G(S) - G(X))\frac{D}{100N_A}\right]$$

$$\frac{1}{M_w} = \frac{1}{M_{w0}} + \left(\frac{G(S)}{2} - 2G(X)\right)\frac{D}{100N_A}$$

where $G(X)$ is the radiochemical yield for crosslinking (almost zero, here), D is the dose in eV ($1\,\mathrm{kGy} = 6.24 \times 10^{18}\,\mathrm{eV\,g^{-1}}$) and N_A is Avogadro's number.

The average values $G(S)$ for each dose are given in *Table 1*. They range between 1.6 and 3.0, which is in good agreement with literature values. They display a clear tendency to decrease with dose which is not surprising since secondary reactions, for instance radical additions to double bonds, are expected to become more and more important as molecular weight decreases.

$G(S)_s$ is systematically higher than $G(S)_u$, the average ratio $G(S)_s/G(S)_u$ being about 1.20 ± 0.1. It can therefore be concluded that tensile loading increases the rate of radiochemical chain scission by a ratio of about 1.2.

DISCUSSION

The above results reveal a low but significant effect of tensile stresses on the radiochemical yield of chain scission. Various tentative explanations can be proposed for this effect.

Mechanochemical chain scissions

According to this hypothesis, skeleton bond cleavage due to high stress concentrations on certain polymer segments would superimpose its effects to those of radiolysis, thus increasing the rate of chain scission. Experimental measurements made on a stressed, non-irradiated sample allowed us to reject this hypothesis: no molecular weight change was observed, showing that 'pure' mechanochemical chain scission is negligible in the conditions under study.

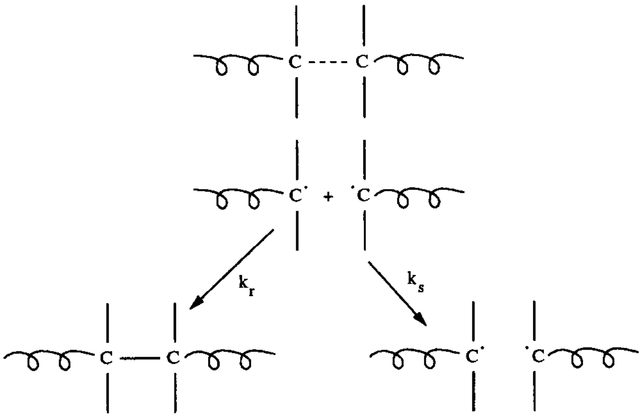


Figure 2 Scheme showing the effects of stress on a primary chain scission

Effect of conformational state on polymer radiolysis

According to Robertson, mechanical loading induces the build-up of the highest energy conformation (HEC) at the expense of the lowest energy one (LEC)[11]. Is the chain scission rate dependent on the conformational state? Concerning first the primary radiolysis, the answer is presumably negative owing to the well-known non-selectivity of radiolytic processes. As seen in the Introduction, however, chain scission results essentially from the rearrangement of primary macroradicals and the yield of this rearrangement could eventually be conformation-dependent.

It is noteworthy that the concentration ratio HEC/LEC is almost constant (frozen) in the glassy state, and increases with temperature above the glass transition temperature (T_g). According to the above hypothesis, $G(S)$ would be expected to vary in the same way with temperature, which seems in contradiction with Wundrich's experimental results[12]. As a matter of fact, the curve $G(S) = f(T)$ experimentally established by this author does not display a noticeable discontinuity at T_g, as expected.

Decrease of the macroradical recombination rate

Practically all authors agree with the hypothesis that the predominant cause of chain scission is the radiolytic cleavage of a lateral bond. However, this hypothesis seems difficult to reconcile with the existence of irradiation-induced changes of the stereostructure[13] and, probably, of the conformational state[14]. These processes presumably need the existence of primary radiolysis of skeleton carbon–carbon bonds. Such events would be, however, very difficult to put in evidence in the case where cage recombination would be highly probable, as expected for PMMA in the glassy state owing to its very low macromolecular mobility.

Here, a stressed chain segment could behave as a spring whose retraction would decrease the probability of recombination as shown schematically in *Figure 2*. A very simple mechanistic scheme could be then proposed:

$$\text{Polymer} \rightarrow [\mathrm{P}^{\cdot} + \mathrm{P}'^{\cdot}]_{\text{cage}} \qquad r_{\mathrm{i}} \text{ (initiation)}$$

$$[\mathrm{P}^{\cdot} + \mathrm{P}'^{\cdot}]_{\text{cage}} \rightarrow \mathrm{P{-}P'} \qquad k_{\mathrm{r}} \text{ (recombination)}$$

$$[\mathrm{P}^{\cdot} + \mathrm{P}'^{\cdot}]_{\text{cage}} \rightarrow \mathrm{P}^{\cdot} + \mathrm{P}'^{\cdot} \qquad k_{\mathrm{s}} \text{ (chain scission)}$$

$$\mathrm{P}^{\cdot} + \mathrm{P}'^{\cdot} \rightarrow \text{Products} \qquad k_{\mathrm{t}} \text{ (non-recombinating termination)}$$

The rate of chain scission $\mathrm{d}n/\mathrm{d}t$ (n = number of moles of chain scissions per unit mass) would be derived from the corresponding kinetic scheme with the stationary-state assumption

$$\frac{\mathrm{d}n}{\mathrm{d}t} = \frac{r_{\mathrm{i}}}{1 + k_{\mathrm{r}}/k_{\mathrm{s}}}$$

r_{i} is presumably independent of temperature and stress and proportional to the radiation intensity as expected for a pure radiolysis event.

k_{r} and k_{s} are dependent on temperature and stress and independent of radiation intensity. $k_{\mathrm{r}}/k_{\mathrm{s}}$ is expected to decrease with temperature (the escape of radicals from the case must be favoured by an increase of macromolecular mobility). $k_{\mathrm{r}}/k_{\mathrm{s}}$ must also decrease with stress intensity according to *Figure 2*. Thus, the chain scission yield (more precisely the contribution of primary skeleton radiolysis to the overall chain scission yield) must be higher in stressed than in unstressed samples, as experimentally observed.

Stress effect on the predominant chain scission process

Let us recall that the predominant chain scission process results from the rearrangement of a macroradical $\mathrm{R}^{\cdot}$ (for instance $\mathrm{R}^{\cdot} = {-}\mathrm{CH_2{-}\dot{C}(CH_3){-}CH_2{-}}$). The following mechanistic scheme could be proposed as a guideline for discussion:

I	Primary radiolysis	Polymer $\rightarrow \mathrm{R}^{\cdot} + \mathrm{E}^{\cdot}$	r_{i}
II	Rearrangement	$\mathrm{R}^{\cdot} \rightarrow$ chain scission	k_{s}
III	Reactions of small radical	$\mathrm{E}^{\cdot} \rightarrow$ products + diffusion	k_{e}
IV	Recombination	$\mathrm{R}^{\cdot} + \mathrm{E}^{\cdot} \rightarrow$ inactive products	k_{t}

It is assumed that the secondary radicals resulting from reactions I and II do not propagate the reaction which seems to be consistent with the kinetic data available on chain scission and with product formation, at least to a first approximation. Here, we consider that chain scission results only from reaction II, so that:

$$\frac{\mathrm{d}n}{\mathrm{d}t} = k_{\mathrm{s}}[\mathrm{R}^{\cdot}]$$

This elementary reaction (scission) is a thermally activated reaction, having presumably a relatively high activation energy E_{S}. It could be imagined that the elastic energy stored in covalent bonds contributes to activation and that, according to Zhurkov *et al.*[15]:

$$E_{\mathrm{ss}} = E_{\mathrm{su}} - V_{\sigma}$$

where E_{SS} and E_{su} are the activation energies relative to, respectively, stressed and unstressed bonds, and V is the so-called activation volume having the dimension of a molar volume. σ is the stress. It can thus be written:

$$k_{\mathrm{ss}} = k_{\mathrm{su}} \exp \frac{V_{\sigma}}{RT}$$

The set of differential equations describing the kinetics of the above mechanistic scheme can be easily resolved on the basis of the hypothesis of stationary state, observing that the apparent order of chain scission is almost zero (the slight decrease of $G(S)$ with dose is neglected in a first approximation). Then:

$$G(S) = \text{constant} \rightarrow [\mathrm{R}^{\cdot}] = \text{constant} \rightarrow \frac{\mathrm{d}[\mathrm{R}^{\cdot}]}{\mathrm{d}t} = 0 \rightarrow \frac{\mathrm{d}[\mathrm{E}^{\cdot}]}{\mathrm{d}t} = 0$$

leading to

$$[\mathrm{R}^{\cdot}] = \frac{k_{\mathrm{e}}}{2k_{\mathrm{t}}}\left(-1 + \sqrt{1 + \frac{4r_{\mathrm{i}}k_{\mathrm{t}}}{k_{\mathrm{e}}k_{\mathrm{s}}}}\right)$$

Let us consider two extreme cases:

(1) $\dfrac{4r_{\mathrm{i}}k_{\mathrm{r}}}{k_{\mathrm{e}}k_{\mathrm{s}}} \ll 1$, then $[\mathrm{R}^{\cdot}] = \dfrac{r_{\mathrm{i}}}{k_{\mathrm{s}}}$ and $\dfrac{\mathrm{d}n}{\mathrm{d}t} = r_{\mathrm{i}}$

It is implicitly considered that the terminating combination (IV) is negligible. In this case, the chain scission yield is proportional to the rate of primary radiolysis and, in principle, independent of stress.

(2) $\dfrac{4r_{\mathrm{i}}k_{\mathrm{r}}}{k_{\mathrm{e}}k_{\mathrm{s}}} \gg 1$, then $[\mathrm{R}^{\cdot}] = \sqrt{\dfrac{r_{\mathrm{i}}k_{\mathrm{e}}}{k_{\mathrm{t}}k_{\mathrm{s}}}}$ and $\dfrac{\mathrm{d}n}{\mathrm{d}t} = \sqrt{\dfrac{r_{\mathrm{i}}k_{\mathrm{e}}}{k_{\mathrm{t}}}}\sqrt{k_{\mathrm{s}}}$

In this case, it can be written:

$$\frac{G(S)_{\mathrm{s}}}{G(S)_{\mathrm{u}}} = \sqrt{\frac{k_{\mathrm{ss}}}{k_{\mathrm{su}}}} = \exp\frac{V\sigma}{2RT} \approx 1.2 \rightarrow V \approx \frac{0.36RT}{\sigma} \approx 19\,\mathrm{cm^3\,mol^{-1}}$$

The pseudo activation volume would be thus about one-fourth of the molar volume of a monomer unit. There is no peculiar physical meaning for this value. As a matter of fact, an important part of the elastic energy is presumably stored in secondary (Van der Waals') bonds responsible for cohesion, so that a rigorous approach to this problem would need to differentiate between inter- and intramolecular stress components, only the latter being active in the activation of scission.

The above scheme is probably not realistic but it allows us to illustrate the general trends of a process in which the elementary step of chain scission would be stress-activated:

(1) stress effects can occur only if the precursor of chain scission (macroradical $\mathrm{R}^{\cdot}$) is also involved in competitive processes (giving no chain scission);
(2) if $\lambda = k_{\mathrm{ss}}/k_{\mathrm{su}}$ is the ratio expressing the stress effect on the elementary step of chain scission, the existence of competitive steps leads systematically to $G(S)_{\mathrm{s}}/G(S)_{\mathrm{u}} < \lambda$; and
(3) for a realistic modelling of stress effects, it seems necessary to distinguish between intra- and intermolecular stress components.

CONCLUSIONS

Our experimental results reveal a small but significant effect of tensile stresses on the rate of radiochemical chain scission in atactic PMMA. The yield of chain scission $G(S)$ is increased by a factor of about 1.2 ± 0.1 for a tensile stress of 47 MPa.

Neither mechanochemical chain scissions nor stress-induced conformational changes seem able to explain the observed behaviour, which is presumably linked to a direct stress effect on radiochemical processes. Two mechanisms have been hypothesized. The first one involves a primary radiolysis of skeleton bonds. Tensile stresses would favour separation of the resulting macroradicals and then increase the chain scission yield by decreasing the recombination rate. The second mechanism involves a primary radiolysis of lateral bonds. Here, the scission of the resulting macroradical would be stress-activated.

The first mechanism appears to be very difficult to study because it concerns only a minority of chain scission events. The second mechanism also presents noticeable difficulties because it needs to take into account secondary reactions, complicating the kinetic scheme and requiring the use of various rate constants as adjustable parameter.

REFERENCES

1 Stepanov, V. F., Vaisberg, S. E. and Karpov, V. L. *Fiziko-Khimicheskaya Mekhanika Materialov* 1968, **4**(1), 30
2 Vaisberg, S. E., Sichkar, V. P., Stepanov, V. F. and Karpov, V. L. *Vysokomol. Soyed A* 1969, **11**, 2577
3 Velikovskii, A. A., Tynnyi, A. N. and Karaiev, V. S. *Fiziko-Khimicheskaya Mekhanika Materialov* 1968, **4**, 448
4 Regel, V. R. and Chernyi, N. N. *Vysokomol. Soyed* 1963, **5**, 925
5 Wall, L. A. and Brown, D. W. *J. Phys. Chem.* 1957, **61**, 129
6 Charlesby, A. 'Atomic Radiation and Polymers', Pergamon Press, Oxford, 1960
7 Todd, A. *J. Polym. Sci.* 1960, **42**, 223
8 David, G., Fuld, D., Geuskens, G. and Charlesby, A. *Eur. Polym. J.* 1969, **5**, 641
9 Kircher, J. F., Sliemers, J. F., Markle, F. A. and Gager, R. A. *J. Phys. Chem.* 1965, **69**, 189
10 Saito, O. *J. Phys. Soc. Jpn* 1968, **13**, 1451
11 Robertson, R. E. *Appl. Poylm. Symp.* 1968, **7**, 201
12 Wundrich, K. *J. Polym. Sci., Polym. Phys. Edn* 1973, **11**, 1293
13 Geuskens, G., Fuld, D. and David, C. *Makromol. Chem.* 1972, **160**, 347
14 Thominette, F. *Thesis*, ENSAM, Paris, 1993
15 Zhurkov, S. N., Zakrevski, V. A., Korsukov, V. E. and Kuksenko, V. S. *J. Polym. Sci. A2* 1972, **10**, 1509