Effect of solvent on the termination step for the radical copolymerization of methyl methacrylate and styrene*

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The kinetics of the radical copolymerization of methyl methacrylate and styrene in benzene, chlorobenzene and benzonitrile has been investigated gravimetrically. The copolymerization termination step is analysed on the basis of the chemically controlled model, the diffusion-controlled model and the combined physical and chemical model, taking into account the corresponding reactivity ratios and the homopolymerization parameters in the three solvents used. The values obtained for the termination step parameters suggest that the termination step might be controlled by the viscosity of the reaction medium, but the sequence distribution and the stereochemical configuration of the polymer chains must also be considered.

INTRODUCTION

The effect of the solvent in free-radical homopolymerization has been described[1–4]. These investigations showed that the termination rate constant appears to be inversely proportional to the viscosity of the medium. The small effects on the propagation rate constant have been attributed to complexing of the propagating radicals with the solvents. Initiation rates are not affected by the presence of the different solvents. However, it has become apparent that the reactivity ratios in free-radical copolymerization are affected, to some extent, by the nature of the reaction medium[1,5–7]. Recently, we have shown that aromatic solvents give rise to an increase in the reactivity ratios of acceptor monomers when the polarity of the solvent increases, whereas, in the same way, the reactivity ratios of the donor monomer decrease[8,9]. These findings are a consequence of the increase, (for acceptor monomers), or decrease, (for donor monomers), of the corresponding homopropagation rate constants when the polarity of the solvent increases[10].

The cross-propagation rate constants, are also affected by solvents. They increase or decrease depending on the electronic acceptor or donor character of the growing radical end, as compared with the electronic character of the monomer molecule that is added to the corresponding radical end[8,9]. The relation between the polarity of the solvents and the variation of the reactivity ratios has been pointed out by other authors[6,7]. The effect of solvents on the kinetics of copolymerization has been stated by Ito and Otsu[5], who showed that the overall rate of copolymerization with the increase of the polar nature of the solvent used. The effect of the solvent on the termination step in free-radical copolymerization, has been studied by Bonta *et al.*[11] taking into account the theoretical approach of Russo and Munari[12].

The termination step kinetics of free-radical copolymerization has been explained by three different mechanisms. The first, suggested by Melville *et al.*[13] and Walling[14], is based upon a chemical-controlled termination and introduces the so-called φ factor defined as:

$$\varphi=\frac{k_{t_{ab}}}{2(k_{t_{aa}}\cdot k_{t_{bb}})^{1/2}}$$

where $k_{t_{aa}}$ and $k_{t_{bb}}$ are the termination rate constants for monomers and $k_{t_{ab}}$ the corresponding cross-termination rate constant.

North *et al.*[15,16] suggested a three-stage consecutive process for the radical termination step. The first two steps (translational diffusion and segmental rearrangement) are diffusion controlled and they are followed by the chemical reaction. North *et al.*[15] suggested an alternative derivation of the copolymer rate equation in which they used a single rate coefficient, $k_{t_{(ab)}}$, to describe the termination reaction.

Russo and Munari[12] combined both physical and chemical aspects into a common scheme and proposed the existence of ten termination reactions referring to four different radicals, $-\mathrm{AA}^{\cdot}$, $-\mathrm{AB}^{\cdot}$, $-\mathrm{BA}^{\cdot}$ and $-\mathrm{BB}^{\cdot}$. They assumed that the cross-termination constants are equal to the geometric mean of the two self-terminations. The copolymer rate equation derived by Russo and Munari[12] is based on a semiquantitative evaluation of the chain end mobility, as compared with the flexibility of inner portions of the chain, and on the assumption that the rate conditioning segmental rearrangement can be limited, from a kinetic point of view, to the last four or five carbon-carbon bonds. They obtained a two parameters equation and the unknown parameters δ_{AB} and δ_{BA} are defined as:

$$\delta_{\mathrm{AB}}=\frac{(k_t^{\mathrm{ab:ba}})^{1/2}}{k_p^{\mathrm{b}}} \quad \text{and} \quad \delta_{\mathrm{BA}}=\frac{(k_t^{\mathrm{ba:ab}})^{1/2}}{k_p^{\mathrm{a}}}$$

where $k_t^{\mathrm{ab:ba}}$ and $k_t^{\mathrm{ba:ab}}$ are the termination rate constants for both the $-$ab and $-$ba, and $-$ba and $-$ab, radicals reactions, respectively, and k_p^{b} and k_p^{a} are the propagation rate constants for the b and a monomers, respectively.

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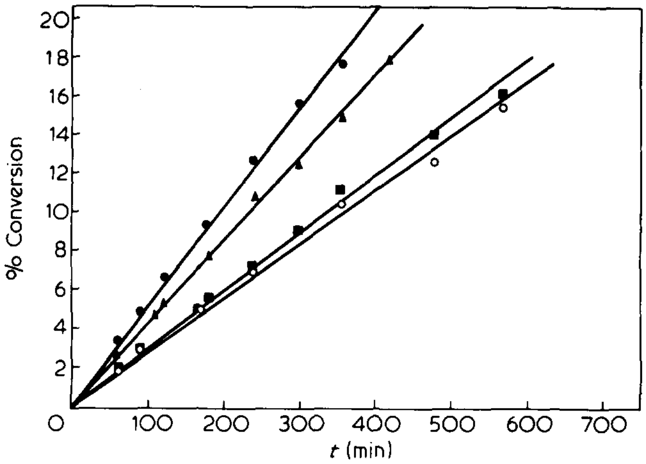

Figure 1 Radical copolymerization of the styrene–methyl methacrylate system in benzene at 60°C. (●) $f_A = 0.20$; (▲) $f_A = 0.30$; (■) $f_A = 0.70$ and (○) $f_A = 0.80$

This paper describes the kinetics of the copolymerization of styrene and methyl methacrylate monomers in benzene, chlorobenzene and benzonitrile. The effect of the solvent on the overall rate of copolymerization is shown and, taking into account the values of kinetic homopolymerization parameters and the reactivity ratios previously obtained[9,10], the copolymerization termination step is studied. The effect of solvent on the values obtained for φ, $k_{t(ab)}$ and δ_{AB} and δ_{BA} are compared and the usefulness of the three theoretical points of view is discussed.

EXPERIMENTAL

Materials

Monomers-styrene and methyl methacrylate; initiator-2,2'azobisisobutyronitrile (AIBN); and solvents-benzene, chlorobenzene and benzonitrile; were purified as described previously[9].

Copolymerization

Reactions were carried out at 60±0.1°C under high vacuum with AIBN as initiator. Monomer and initiator concentrations were 3 mol l^{-1} and 0.3 mol % of the total monomer concentration, respectively. Rates of copolymerization were measured gravimetrically and conversion of monomer to copolymer was limited to a maximum of 20% such that calculated copolymer and monomer drifts were limited to less than 2–3%. Viscosities of monomer–solvent mixtures were measured using a suspended level viscometer. Isolation of copolymers and other experimental conditions have been described[9].

RESULTS

Overall rate of free-radical copolymerization

Figure 1 shows the relation between conversion percentage and reaction time for different monomer feed compositions, when free-radical copolymerization is carried out in benzene. Similar plots are obtained when chlorobenzene or benzonitrile is used as solvent. Rates of copolymerization were obtained from the slopes of straight lines taking into account the overall monomer concentrations in the feed.

As shown in *Table 1*, the overall rate of copolymerization is higher when the methyl methacrylate molar fraction in the feed increases, being independent of the solvent used in the copolymerization. In agreement with results published by Ito and Otsu[5], for any one feed composition the overall rate of copolymerization increases when the solvent polarity increases. As shown in *Figure 2*, straight lines were found in the plot of the overall rate of copolymerization *versus* dielectric constant of the corresponding solvents.

Termination step in free-radical copolymerization

Previously[10] we found that when AIBN is used as initiator, the rates of initiation in the free-radical homopolymerization of methyl methacrylate are slightly different from those obtained in the free-radical homopolymerization of styrene, both being practically independent of the solvent used. The values of the initiation rate of copolymerization for the different monomer feed com-

Table 1 Polymerization rates for the system styrene–methyl methacrylate at 60°C in solution. $[A]_0 + [B]_0 = 3$ mol l^{-1}, [AIBN] = 0.3 mol %

Solvent	f_A*	$R_p \cdot 10^{-6}$ (mol dm^{-3} s^{-1})
Benzene	1.00	13.5
	0.80	7.8
	0.70	8.7
	0.60	9.9
	0.50	11.1
	0.40	12.0
	0.30	12.3
	0.20	15.0
	0.00	84.0
Chlorobenzene	1.00	17.1
	0.80	9.6
	0.70	10.2
	0.60	9.9
	0.50	10.8
	0.40	11.4
	0.30	14.1
	0.20	16.2
	0.00	90.0
Benzonitrile	1.00	17.7
	0.80	11.7
	0.70	13.5
	0.60	14.1
	0.50	17.4
	0.40	20.0
	0.30	21.0
	0.20	25.8
	0.00	120.0

* Molar fraction of styrene in the feed

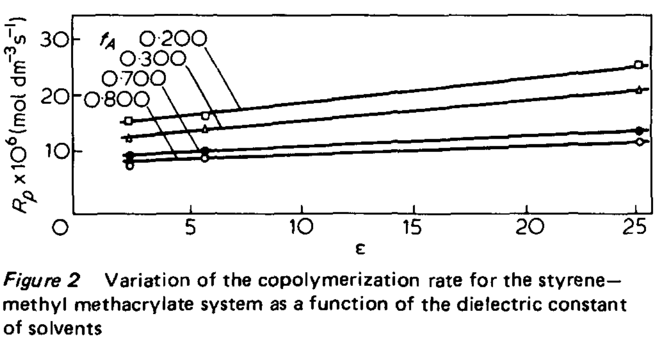

Figure 2 Variation of the copolymerization rate for the styrene–methyl methacrylate system as a function of the dielectric constant of solvents

Table 2 Kinetic parameters for the termination step of the radical copolymerization of styrene and methyl methacrylate in solution

Solvent	f_A*	F_A†	ϕ	$k_{t(ab)}\cdot 10^{-8}$ (dm^{-3} mol^{-1} s^{-1}	ϕ Average	$k_{t(ab)}\cdot 10^{-8}$ (Average) (dm^{-3} mol^{-1} s^{-1})
Benzene	0.200	0.307	29.2	6.81	53.3	7.54
	0.300	0.373	34.4	9.18		
	0.700	0.638	67.8	7.51		
	0.800	0.741	81.8	6.66		
Chlorobenzene	0.200	0.264	39.8	7.08	53.1	7.61
	0.300	0.359	43.5	8.47		
	0.700	0.652	60.3	7.56		
	0.800	0.708	69.0	5.34		
Benzonitrile	0.200	0.249	25.9	3.35	41.3	3.85
	0.300	0.315	34.7	4.41		
	0.700	0.597	45.6	4.04		
	0.800	0.686	58.9	3.61		

* Molar fraction of styrene in the feed
† Molar fraction of styrene in the copolymer

positions have been obtained through a linear interpolation. These values together with those of the reactivity ratios and the ratios $\delta = k_t^{1/2}/k_p$ (where k_t and k_p are the rate constants for the homotermination and homopropagation, respectively) in the different solvents, which are necessary to calculate the three parameters included in the mechanisms, have been taken from our previously published data[9,10].

The φ factor has been calculated from equation[16]:

$$R_p = \frac{(r_A[A]^2 + 2[A]\cdot[B] + r_B[B]^2)R_i^{1/2}}{(r_A^2\delta_A^2[A]^2 + 2\varphi r_A r_B \delta_A \delta_B[A][B] + r_B^2\delta_B^2[B]^2)^{1/2}} \tag{1}$$

where [A] and [B] are the molar concentrations of styrene and methyl methacrylate in the feed, respectively, r_A and r_B are the reactivity ratios and R_i the initiation rate.

The $k_{t(ab)}$ parameter has been calculated from equation[16]:

$$R_p = \frac{(r_A[A]^2 + 2[A][B] + r_B[B]^2)R_i^{1/2}}{k_{t(ab)}^{1/2}\left(r_A\frac{[A]}{k_{p_{aa}}} + r_B\frac{[B]}{k_{p_{bb}}}\right)} \tag{2}$$

where $k_{p_{aa}}$ and $k_{p_{bb}}$ are the propagation rate constants of styrene and methyl methacrylate respectively. The values of φ and $k_{t(ab)}$ for each composition are quoted in *Table 2.*

The unknown parameters δ_{AB}^0 and δ_{BA}^0, which are defined as indicated above, but taking into account the dependence upon the viscosity of the mixture (η_{mix}) of the various termination rate coefficients, have been obtained from equation (3) in which $x = [A]/[B]$

$$R_p = R_i^{1/2}[B]\eta_{mix}^{1/2}\left[\frac{r_A^2x^3 + 3r_Ax^2 + 2x + r_Ar_Bx + r_B}{r_A^2x^2\,\delta_A^0 + r_A\,x\,\delta_{BA}^0 + \frac{r_Bx(r_Ax+1)}{r_B+x}\delta_{AB}^0 + \frac{r_B^2(r_Ax+1)}{r_B+x}\delta_B^0}\right] \tag{3}$$

This equation is a modified Russo and Munari equation, proposed by Bonta *et al*[7]. δ_A^0 and δ_B^0 are the homopolymerization parameters δ_A and δ_B, corrected by the viscosity of the reaction medium. The obtained values are quoted in *Table 3.*

Table 3 Calculated values of δ parameters for the termination step of the radical copolymerization of styrene and methyl methacrylate in solution

	Solvent		
	Benzene	Chloro-benzene	Benzoni-trile
δ_A^0 (mol$^{1/2}$ s$^{1/2}$ dm$^{-3/2}$ cp$^{1/2}$)	27.3	25.5	31.0
δ_B^0 (mol$^{1/2}$ s$^{1/2}$ dm$^{-3/2}$ cp$^{1/2}$)	6.33	6.23	5.31
δ_{BA}^0 (mol$^{1/2}$ s$^{1/2}$ dm$^{-3/2}$ cp$^{1/2}$)	105	128	121
δ_{AB}^0 (mol$^{1/2}$ s$^{1/2}$ dm$^{-3/2}$ cp$^{1/2}$)	66	60	49
δ_{BA}^0/δ_A^0	3.8	5.0	3.9
δ_{AB}^0/δ_B^0	10.4	9.6	9.2

1 cp = 10^{-2} g cm^{-1} s^{-1}

The ratios δ_{BA}^0/δ_A^0 and δ_{AB}^0/δ_B^0 are equal to the square roots of the ratios between the corresponding termination rate constants, i.e. $(k_t^{ba:ab}/k_t^{aa:aa})_0^{1/2}$ and $(k_t^{ab:ba}/k_t^{bb:bb})_0^{1/2}$ being independent of the viscosity of the medium. In agreement with Bonta *et al.*[7], if each termination rate constant is a function of the flexibility of the corresponding chain end, it is reasonable to assume that the above ratios do not include any difference in chemical reactivity since the same terminal unit is involved in each case and the methyl methacrylate–styrene system does not have penultimate effects in the chemical sense. Therefore, δ_{BA}^0/δ_A^0 and δ_{AB}^0/δ_B^0 are a measure of the difference in flexibility only. The values obtained for δ_{BA}^0/δ_A^0 and δ_{AB}^0/δ_B^0 are also quoted in *Table 3.*

As observed in *Table 2*, the so-called φ factor changes with the monomer feed composition reaching higher values when the styrene fraction in the feed increases. This behaviour has been observed in all the solvent used and similar results have been described for methyl methacrylate–styrene systems[14,17,18]. However, φ takes different values for the same feed composition in the three solvents, which is a first indication of the effect of solvents in the copolymerization termination step.

The $k_{t(ab)}$ parameter also changes with the monomer feed compositions and the highest values of $k_{t(ab)}$ correspond to intermediate feed compositions. The variation of $k_{t(ab)}$ parameter for each solvent with the monomer composition could be explained taking into account that the copolymer chemical composition could modify the chain flexibility and coil dimensions giving rise to a

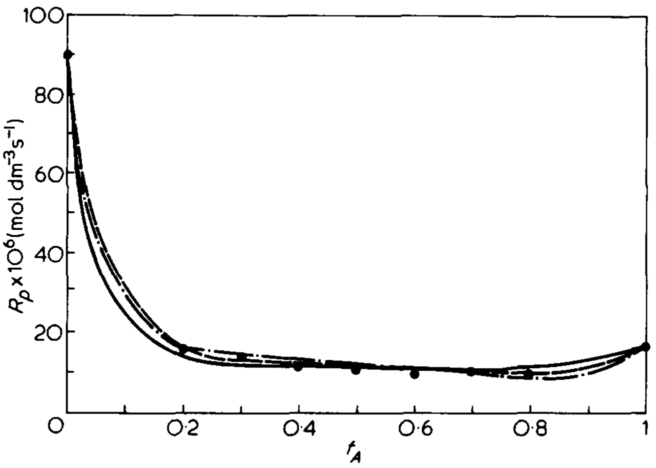

Figure 3 Comparison between experimental results and theoretical curves of the copolymerization rate for the styrene–methyl methacrylate system in benzene. (——), Walling; (– - –), North; (– – – –), Russo *et al.*

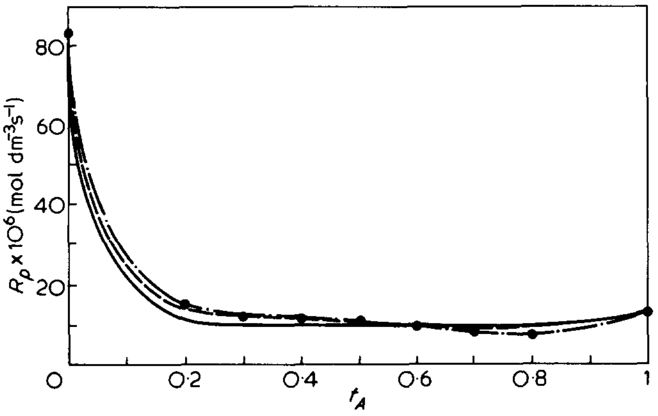

Figure 4 Comparison between experimental results and theoretical curves of the copolymerization rate for the styrene–methyl methacrylate system in chlorobenzene. Lines as for ***Figure 3***

modification of the segmental diffusion coefficient which are the controlling steps in the North diffusion theory.

However, if the $k_{t(ab)}$ values obtained for the same monomer feed composition in the different solvents are compared, the differences in the copolymer chemical composition are not great enough to account satisfactorily for the differences found in the $k_{t(ab)}$ values. As stated previously[9,19] the solvent affects the reactivity ratios of methyl methacrylate–styrene system and the sequence distribution and the steroechemical configuration of the copolymers. When the polarity of the solvent is higher, the molar triad fraction of MMM (where M refers to methyl methacrylate) increases, whereas the molar triad fraction of SMS (where S refers to styrene) decreases and molar triad fractions of SMM (or MMS) increase up to 70 mole % of methyl methacrylate feed composition[19]. However, the stereochemical configuration of copolymer is changed and an increase of polarity of the solvent favours a coisotactic configuration of the different triads[19]. It is to be expected that this fact affects the chain flexibility and the observed variation in the $k_{t(ab)}$ values might be related to these phenomena.

An indication of the chain end flexibility could be obtained from δ^0_{BA}/δ^0_A and δ^0_{AB}/δ^0_B. The δ values shown in *Table 3* are higher than unity indicating that chain end flexibility is higher when the penultimate and ultimate units differ. Also, the effects are stronger when the penultimate unit of the two methyl methacrylate consecutive units in the growing radical end are replaced by a styrene unit. These findings agree with the O.Driscoll[20] and Bonta[11] data. However, Bonta *et al.*[11] have found that when methyl methacrylate and styrene are copolymerized in acetone, dimethylformamide and dioxane, similar values of δ^0_{BA}/δ^0_A and δ^0_{AB}/δ^0_B ratios are obtained, inde- the solvent used. The values in *Table 3* change from one solvent to another, indicating that the sequence distribution and the stereochemical configuration have an important role in the free-radical copolymerization termination step.

The corresponding theoretical curves of the overall rates of copolymerization as a function of the styrene molar fraction in the monomer feed, have been drawn in *Figures 3–5*, following equations (1)–(3), respectively, taking the average values of the φ factor and the $k_{t(ab)}$ parameter as well as the values of δ^0_{BA} and δ^0_{AB} parameters. The agreement between experimental and theoretical values is rather poor for the chemical-controlled termination theory in all the solvents used, but a qualitative concordance is obtained for the North diffusion theory and for the physical and chemical control proposed by Russo and Munari, although more qualitative information can be obtained from the Russo and Munari theory.

At present, the free-radical termination step in homopolymerization is being investigated in detail[21-23]. Most papers indicate that the conformation of chain, which is dependent on the thermodynamic properties of the solvent, has a great effect on the termination rate coefficient[22]. However, molecular weight and concentration of polymer have also been shown to affect the termination rate coefficient[21,22]. The proposed theoretical treatments applied in this paper do not take into consideration all the above mentionated factors. Investigations are in progress for a more quantitative approach.

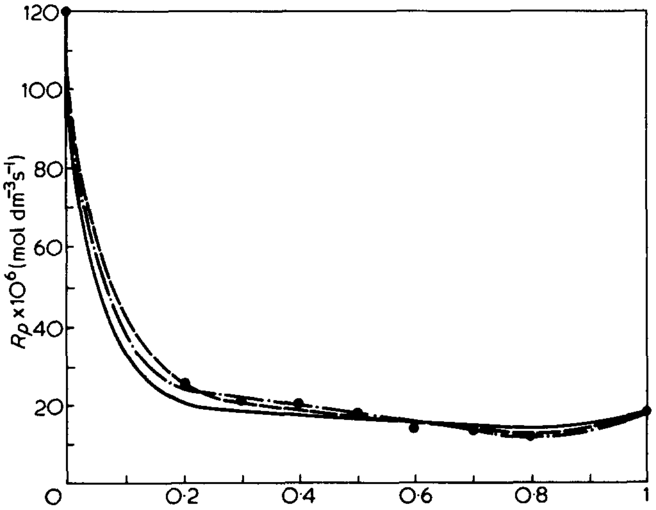

Figure 5 Comparison between experimental results and theoretical curves of the copolymerization rate for the styrene–methyl methacrylate system in benzonitrile. Lines as for ***Figures 3*** and ***4***

REFERENCES

1 Bamford, C. H. in 'Molecular Behaviour and the Development of Polymeric Materials' (Eds. A. Ledwith and A. M. North) Chapman and Hall, London, 1975

2 Scott, G. E. and Senogles, E. *J. Macromol. Sci. Revs. Macromol. Chem.* 1973, **C-9**, 49

3 Kamachi, M., Satoh, J., Liaw, D. J. and Nozakura, S. *Macromolecules* 1977, **10**, 501

4 Kamachi, M., Liaw, D. J. and Nozakura, S. *Polym. J.* 1977, **9**, 307

5 Ito, T. and Otsu, T. *J. Macromol. Sci. Chem.* 1969, **A3**, 197

6 Cameron, G. G. and Esslemont, G. F. *Polymer* 1972, **13**, 435

7 Bonta, G., Gallo, M. and Russo, S. *Polymer* 1975, **16**, 429

8 Madruga, E. L., San Román, J. and Gumán, J. *J. Macromol. Sci. Chem.* 1979, **A13**, 1089

9 Madruga, E. L., San Román, J. and Del Puerto, M. A. *J. Macromol. Sci. Chem.* 1979, **A13**, 1105

10 Madruga, E. L., San Román, J. and Del Puerto, M. A. *Anal. Quim. (R.S.E.F.Q.)* 1979, **75**, 294

11 Bonta, G., Gallo, M. and Russo, S. *J. Chem. Soc. Faraday Trans. I.* 1975, **71**, 1727

12 Russo, S. and Munari, S. *J. Macromol. Sci. Chem.* 1968, **A2**, 1321

13 Melville, H. W., Noble, B. and Watson, W. F. *J. Polym. Sci.* 1947, **2**, 229

14 Walling, C. *J. Am. Chem. Soc.* 1949, **71**, 1930

15 Atherton, J. N. and North, A. M. *Trans. Faraday Soc.* 1962, **58**, 2049

16 North, A. M. 'Kinetics of Free-Radical Polymerization', Pergamon Press, Oxford, 1966

17 Bevington, J. C., Melville, H. W. and Taylor, R. P. *J. Polym. Sci.* 1954, **14**, 463

18 Suzuki, M., Miyama, H. and Fujimoto, S. *J. Polym. Sci.* 1959, **37**, 533

19 San Román, J., Madruga, E. L. and Del Puerto, M. A. *Angew. Makromol. Chem.* 1980, **86**, 1

20 O'Driscoll, K. F., Wertz, W. and Husar, A. *J. Polym. Sci. A-1* 1967, **5**, 2159

21 Mahabadi, H. K. and O'Driscoll, K. F. *Macromolecules* 1977, **10**, 55

22 Mahabadi, H. K. and O'Driscoll, K. F. *J. Polym. Sci. Polym. Lett. Edn.* 1978, **16**, 351

23 Mahabadi, H. K. and Rudin, A. *J. Polym. Sci. Polym. Chem. Edn.* 1979, **17**, 1801