Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Free Radical Copolymerization of ω-(*p*-Vinylbenzyl Ether) Macromonomer of Poly(2,6-Dimethyl-1,4- Phenylene Oxide) with Methyl Methacrylate in the Presence of Different Initiators

Virgil Percec[a]; James H. Wang[a]
[a] Department of Macromolecular Science, Case Western Reserve University Cleveland, Ohio, U.S.A.

To cite this Article Percec, Virgil and Wang, James H.(1991) 'Free Radical Copolymerization of ω-(*p*-Vinylbenzyl Ether) Macromonomer of Poly(2,6-Dimethyl-1,4- Phenylene Oxide) with Methyl Methacrylate in the Presence of Different Initiators', Journal of Macromolecular Science, Part A, 28: 11, 221 — 231

To link to this Article: DOI: 10.1080/00222339108054404

URL: http://dx.doi.org/10.1080/00222339108054404

MACROMOLECULAR REPORTS, A28(SUPPL. 3), 221-231 (1991)

FREE RADICAL COPOLYMERIZATION OF ω-(*p*-VINYLBENZYL ETHER) MACROMONOMER OF POLY(2,6-DIMETHYL-1,4-PHENYLENE OXIDE) WITH METHYL METHACRYLATE IN THE PRESENCE OF DIFFERENT INITIATORS

Virgil Percec* and James H. Wang
Department of Macromolecular Science
Case Western Reserve University
Cleveland, Ohio 44106-2699
U. S. A

ABSTRACT

The free radical copolymerization of ω-(*p*-vinylbenzyl ether) macromonomer of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-VBE, M_2, $\overline{M}_n$ = 18300 g/mol, $\overline{M}_w/\overline{M}_n$ = 1.19) with methyl methacrylate (MMA, M_1) initiated with dicumyl peroxide, di-*tert*-butyl peroxide, and 2,2'-azobisisobutyronitrile (AIBN) was investigated. The determined reactivity ratio of MMA, r_1, was 0.71 and 0.72 for the copolymerizations using di-*tert*-butyl peroxide and respectively dicumyl peroxide. For the copolymerization initiated by AIBN, the r_1 was 0.86. No definitive explanation for the difference between the determined reactivity ratios is reached. Speculations are discussed based on the copolymerization kinetic parameters and the possible correlations with the side reactions in which primary radicals derived from initiators may participate, and with the difference between the onset of the micelle formation.

INTRODUCTION

Macromonomers are ideal precursors for the synthesis of well-defined graft copolymers.[1-8] The graft copolymers prepared by the macromonomer technique have been investigated for such applications as non-ionic surface modifiers,[9-12] durable membranes,[13] solid polymer electrolytes,[14] emulsifiers for incompatible polymer blends,[15] as additives for polymers,[16] etc.

The graft length of the resulting graft copolymers is conveniently controlled by the molecular weight of the macromonomer. However, the number of the grafts on the polymer backbone is determined both by the feed ratio between macromonomer and comonomer, and by the "reactivity" of the macromonomer. Previous results from our laboratory have demonstrated that the "reactivity" of ω-(*p*-vinylbenzyl ether) macromonomer of poly(2,6-dimethyl-1,4-phenylene oxide) (PPO-VBE) depends on the molecular weight of the macromonomer,[17] on the total monomer concentration,[18,19] and on the nature of the polymerization solvent.[18] The concentration and solvent effects were interpreted based on a micelle formation model which causes the partition of the comonomer concentration between the bulk of the solvent and around the growing chain.[18,19]

Recently, it has been demonstrated that the primary radicals derived from radical initiators undergo not only addition to monomers, but also hydrogen abstraction, aromatic substitution, and fragmentation reactions.[20-22] These side reactions introduce various defect groups into the polymers and may eventually deteriorate the stability and the properties of the polymers.[23] It is therefore of interest to investigate whether the copolymerization of a macromonomer and vinyl monomer is significantly affected by the nature of the free radical initiator.

This paper describes the copolymerization of PPO-VBE macromonomer with methyl methacrylate initiated by dicumyl peroxide, di-*tert*-butyl peroxide and 2,2'-azobisisobutyronitrile.

EXPERIMENTAL

MATERIALS

Methyl methacrylate (MMA, 99%, Aldrich) was first washed with 10% NaOH aqueous solution to remove the inhibitor, then with distilled water, dried over anhydrous $CaCl_2$, and distilled under vacuum. Dicumyl peroxide (Polysciences) and di-*tert*-butyl peroxide (98%, Aldrich) were used as received. 2,2'-Azobisisobutyronitrile (AIBN, Fluka) was freshly recrystallized from methanol below 40°C. Tetrahydrofuran (THF) was distilled from $LiAlH_4$. *p*-Chloromethylstyrene (Seimi Chemical, Kanagawa, Japan) was used as received.

TECHNIQUES

The conversion of PPO-VBE macromonomer was determined by gel permeation chromatography (GPC). GPC measurements were performed on a Perkin-Elmer series 10 LC instrument equipped with an LC-100 column oven, an LC 600 autosampler, and a Nelson Analytical 900 series data station. The measurements were made using a UV detector set at 254 nm, THF as solvent (1 mL/min, 40°C), a set of PL-gel columns of 10^2, 5 X 10^2, 10^3, 10^4, and 10^5Å, and a calibration plot constructed with polystyrene standards (Supelco). The conversion of methyl methacrylate (MMA) was determined by gas chromatography (GC). The GC analyses were carried out with a Hewlett-Packard HP 5890A gas chromatograph equipped with a HP 3392A integrator and an SP 1000 column (carbowax 20 and terephthalic acid derivative, Supelco). The temperatures of the oven, injector, and detector were 110, 150, and 150 °C, respectively.

Synthesis of PPO-VBE Macromonomer

Poly(2,6-dimethyl-1,4-phenylene oxide) with a 2,6-dimethylphenol chain end (PPO-OH) was synthesized by a phase transfer catalyzed (PTC) polymerization of 4-bromo-2,6-dimethylphenol as previously described.[24] PPO-VBE macromonomer was synthesized by a PTC etherification of the 2,6-dimethylphenol chain end with *p*-chloromethylstyrene.[17] The crude PPO-VBE macromonomer was fractionated as previously reported.[17] The particular PPO-VBE macromonomer fraction used in this study has $\overline{M}_n$ = 18300 g/mol and $\overline{M}_w/\overline{M}_n$ = 1.19.

Free Radical Copolymerization of PPO-VBE Macromonomer with MMA

The copolymerization technique was described previously in detail.[17-18] The reactivity ratio of MMA (r_1) was determined from the slope of $-\log\{[M_1]_t/[M_1]_0\}$ versus $-\log\{[M_2]_t/[M_2]_0\}$, i.e. the Jaacks' integrated single experiment method.[25]

RESULTS AND DISCUSSION

The free radical copolymerization of PPO-VBE macromonomer (M_2) with MMA (M_1) is outlined in Scheme I. The copolymerization experiments were performed in tetrahydrofuran (THF), using dicumyl peroxide, di-*tert*-butyl peroxide and respectively 2,2'-azobisisobutyronitrile initiators. The copolymerization conditions and the determined reactivity ratios, r_1, of MMA are summarized in Table I. Although dicumyl peroxide and di-*tert*-butyl peroxide are usually used at higher polymerization temperatures,[22] the present copolymerization experiments were performed at 60°C in order to compare these experiments with those resulted from initiation with 2,2'-azobisisobutyronitrile (AIBN).

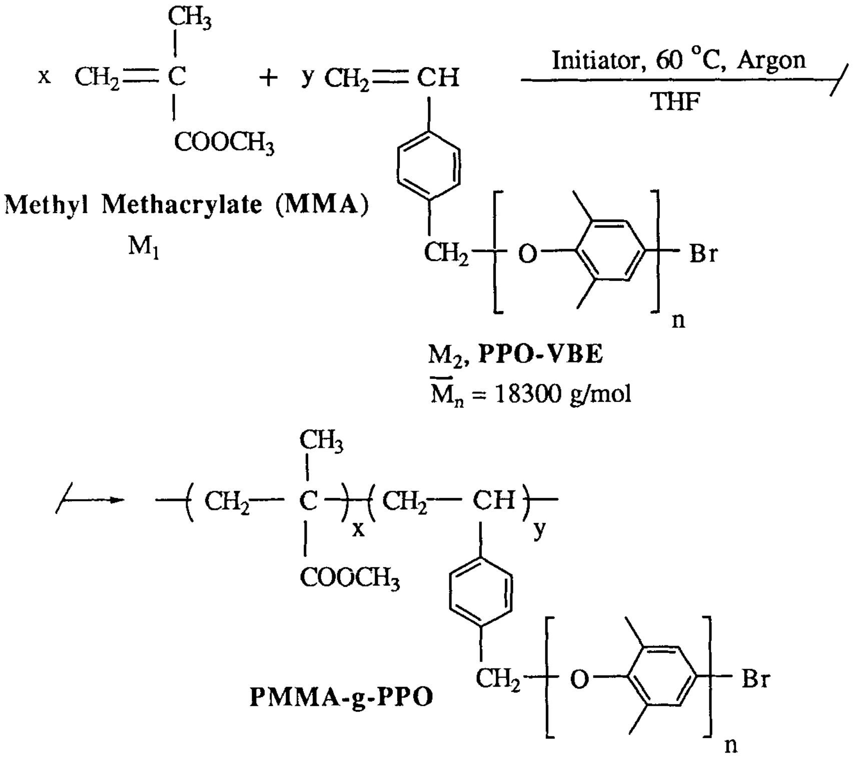
All the copolymerization experiments were carried out at $M_1/M_2 \approx 610$ (mol/mol). The macromonomer concentration, $[M_2]$,

TABLE I
The Reactivity Ratios of M_1 (MMA, r_1) as Determined from the Copolymerization of PPO-VBE (M_2, $\overline{M}_n$ = 18300g/mol; $\overline{M}_w/\overline{M}_n$ = 1.19) with MMA Initiated by Three Different Free Radical Initiators. Polymerization Temperature, 60 °C; Polymerization Solvent, THF).

Free Radical Initiator	M_1 (g)	M_2 (g)	Initiator (mg)	THF (g)	$\frac{[M_1]}{[M_2]}$ (mol/mol)	$[M_2]$ ($X10^{-3}$ mol/L^{-1})	r_1	$\overline{n}_1$ $(r_1 \frac{[M_1]}{[M_2]} + 1)$	$\overline{M}_n$ of Graft Copolymer (GPC) (g/mol)	Calculated $\overline{M}_n$ of Graft Copolymer Repeat unit[a] (g/mol)	$\overline{n}_1{}'$[b]
Dicumyl Peroxide	1.015	0.304	24	3.988	611	3.703	0.72	440	59300	62300	410
Di-*tert*-Butyl Peroxide	1.012	0.303	12	3.982	611	3.692	0.71	436	46000	61900	276
2,2'-Azobisisobutyronitrile	1.016	0.303	14	3.991	614	3.675	0.86	589	47300	71000	290

a) The calculated $\overline{M}_n$ of the graft copolymer repeat unit = M (1) X $\overline{n}_1$ + $\overline{M}_n$ (2), where M (1) = Molecular weight of MMA and $\overline{M}_n$ (2) = $\overline{M}_n$ of PPO-VBE (18300 g/mol).

b) $\overline{n}_1{}' = \frac{\overline{M}_n \text{ (Graft Copolymer)} - \overline{M}_n(2)}{M(1)}$.



Initiator = Dicumyl Peroxide;
2,2'-Azobisisobutyronitrile;
Di-*tert*-butyl Peroxide.

Scheme I. Free radical copolymerization of PPO-VBE macromonomer (M_2) with methyl methacrylate (M_1).

was maintained close to 3.690 X 10^{-3} mol/L. Under these conditions, the propagation through the macroradical, $M_2\cdot$ can be neglected and therefore, the Jaacks' integrated single experiment method is applicable to the determination of r_1.[25] The reactivity ratios of MMA, r_1, are 0.72 and 0.71 respectively for the copolymerizations initiated by dicumyl peroxide and di-*tert*-butyl peroxide. Within the experimental error, the reactivity ratios are the same for these

$$M_1 = \text{MMA} \qquad M_2 = \text{PPO-VBE}$$

$$-\frac{d[M_1]}{dt} = k_{11}[M_1^\bullet][M_1] + k_{21}[M_2^\bullet][M_1] \qquad (1)$$

$$-\frac{d[M_2]}{dt} = k_{12}[M_1^\bullet][M_2] + k_{22}[M_2^\bullet][M_2] \qquad (2)$$

Since $[M_1] >> [M_2]$

$$k_{21}\,[M_2^\bullet][M_1] \approx 0 \qquad (3)$$

$$k_{22}\,[M_2^\bullet][M_2] \approx 0 \qquad (4)$$

$$-\frac{d[M_1]}{dt} \approx k_{11}[M_1^\bullet][M_1] \approx k_{11}[M_1^\bullet]_{ss}\,[M_1] \qquad (5)$$

$$-\ln\frac{[M_1]_t}{[M_1]_0} = k_{11}[M_1^\bullet]_{ss}\,t \qquad (6)$$

$$-\frac{d[M_2]}{dt} \approx k_{12}[M_1^\bullet][M_2] \approx k_{12}[M_1^\bullet]_{ss}\,[M_2] \qquad (7)$$

$$-\ln\frac{[M_2]_t}{[M_2]_0} = k_{12}[M_1^\bullet]_{ss}\,t \qquad (8)$$

Scheme II. An analysis of the copolymerization kinetics.

copolymerizations using the two peroxide initiators. However, the r_1 determined from the copolymerization experiment using AIBN is 0.86.

An analysis of the copolymerization kinetics is presented in Scheme II. The rates of the comonomers consumption are represented by eqs 1 and 2. Since $[M_1] \approx 610 \times [M_2]$, the propagation through the macroradical $M_2\cdot$ can be neglected. This results in eqs 3 and 4. Consequently, eq 1 is reduced to eq 5. If $[M_1\cdot]$ maintains a steady state concentration ($[M_1\cdot]_{ss}$), the integration of eq 5 leads to eq 6. This allows the estimation of $k_{11}[M_1\cdot]_{ss}$ from the slope of the plot $-\ln([M_1]_t/[M_1]_o)$ versus polymerization time. Eq 8 is similarly derived by the integration of eq 7. From the slope of the plot $-\ln([M_2]_t/[M_2]_o)$ versus polymerization time, we calculated $k_{12}[M_1\cdot]_{ss}$. These slopes were determined and are summarized in Table II. The $k_{11}[M_1\cdot]_{ss}$

TABLE II

A Summary of the Copolymerization Kinetic Parameters as Determined from the Free Radical Copolymerization of Methyl Methacrylate (M_1) and PPO-VBE (M_2, $\overline{M}_n$ = 18300 g/mol; $\overline{M}_w/\overline{M}_n$ = 1.19). Polymerization Temperature, 60 °C; Polymerization Solvent, THF.

	Initial Monomer Concentration		Slope of the plot -log ($[M_i]_t/[M_i]_o$) versus polymerization time plot	
Free Radical Initiator	$[M_1]_o$ (mol/L)	$[M_2]_o$ (10^{-3} mol/L)	$k_{11}[M_1\bullet]_{ss}$[a] (10^{-5} s^{-1})	$k_{12}[M_1\bullet]_{ss}$[b] (10^{-5} s^{-1})
Dicumyl Peroxide	2.225	3.703	0.81	1.21
Di-*tert*-butyl Peroxide	2.249	3.692	1.67	1.80
2,2'-Azobisisobutyronitrile	2.253	3.675	1.77	2.46

a) $k_{11}[M_1\bullet]_{ss}$ is determined from the slope of the plot -log ($[M_1]_t/[M_1]_o$) versus polymerization time, where $[M_1\bullet]_{ss}$ is the steady state concentration of the radical $M_1\bullet$.

b) $k_{12}[M_1\bullet]_{ss}$ is determined from the slope of the plot -log ($[M_2]_t/[M_2]_o$) versus polymerization time, where $[M_1\bullet]_{ss}$ is the steady state concentration of the radical $M_1\bullet$.

and $k_{12}[M_1\cdot]_{ss}$ values correspond approximately to the pseudo rate constants by which comonomers M_1 and M_2 are consumed. In all cases, M_2 is consumed faster than M_1. This is expected since the reactivity of the *p*-vinylbenzyl group of M_2 is higher than that of MMA. The $k_{12}[M_1\cdot]_{ss}$ value for the experiment with AIBN is higher than those with dicumyl peroxide and di-*tert*-butyl peroxide.

At the present, we do not have a reasonable explanation for the difference between the determined r_1 values using different initiators. The most probable reasons are discussed below.

Although these copolymerizations were performed with the same molar ratio of monomer to initiator, the number average molecular weights ($\overline{M}_n$) of the resulting graft copolymer are quite different. This may be caused by the difference between the initiator efficiencies and by the difference between the side reactions of the primary radicals derived from the initiators.[20] Beside the expected addition of the primary radical to the monomer, 2-cyano-2-propyl radical derived from AIBN was found to undergo side reactions leading to methacrylonitrile, isobutyronitrile, ketenimine, etc.[26]

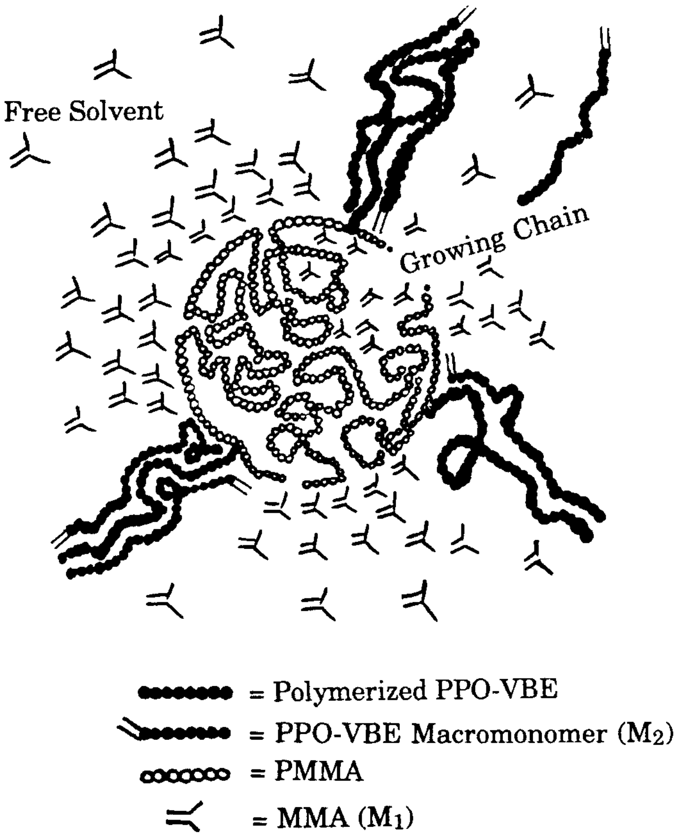


Figure 1. Schematic representation of the micelle formation model.

These side reactions reduce significantly the initiator efficiency. However, no hydrogen abstraction reaction from the monomer was observed for the AIBN derived radical.[26]

As determined from radical trapping experiments, during the polymerization of MMA, only 51% of the primary cumyloxy radicals undergo the desired addition to the monomer. As much as 21% and 23% of the cumyloxy radicals participate in hydrogen abstractions from both the α-methyl and the ester methyl groups and respectively in the β-scission to produce the secondary methyl radical.[27] Similarly, only 63% of the primary *tert*-butoxy radicals undergo addition to MMA, while 21% and 23% of *tert*-butoxy radicals participate in hydrogen abstraction and β-scission reactions.[28] In the copolymerization of styrene with MMA, the cumyloxy and *tert*-butoxy radicals have higher rate constant of addition to styrene than that of addition to MMA. However, the secondary methyl radicals derived from β-scission have lower rate constant of the addition to styrene versus MMA.[21,28]

The copolymerization of PPO-VBE macromonomer with MMA and butyl methacrylate were proposed to involve the formation of micelles due to the difference in the solubilities of PPO graft and the PMMA backbone in the polymerization solvents (Figure 1).[18,19] The micelle formation leads to the partition of the comonomer concentrations between the bulk of the solvent and around the growing chain. This non-ideal concentration effect causes the determined "reactivity", $1/r_1$, of the PPO-VBE macromonomer (M_2) to depend on experimental conditions such as comonomer concentration and nature of the polymerization solvent.

Since above a certain degree of polymerization (DP) the PMMA chain of the growing graft copolymer (containing a PPO graft) forms micelles, the difference between the rates of addition of the primary radical to the *p*-vinylbenzyl (i.e. styrene-like) end group of the macromonomer (M_2) versus that to MMA may cause the difference between the onset of the micelle formation. Because the formation of micelles requires the presence of PPO graft derived from M_2, we would speculate that the initiators with higher rate constant of addition to the *p*-vinylbenzyl end group than that to MMA could have an early onset of the micelle formation. The cumyloxy, tert-butoxy and 2-cyano-2-propyl radicals have the ratio of $k_{MMA}/k_{styrene}$ of 1/10,[28] 1/5,[21] and 1/2[29] respectively. This indicates that the cumyloxy and tert-butoxy radicals have higher rate constants than 2-cyano-2-propyl radical of addition to styrene versus MMA. An early onset of micelle formation and lower r_1 values[18,19] are expected for the two peroxide initiators versus AIBN. However, the rate of the addition is actually governed by the product of the rate constant and the concentration. Since $[M_1] \approx 610 \times [M_2]$, the difference between the rate of addition to MMA vs. styrene end group is still dominated by the concentration of the comonomers. The complete understanding of the reasons for the difference between the determined reactivity ratios requires more kinetic experiments to isolate and examine each of the most probable factors. Nevertheless the fact that the nature of the radical initiator may affect the "reactivity" of the macromonomers should be carefully considered and therefore deserves further research.

ACKNOWLEDGMENTS

Acknowledgment is made to the donors of the Petroleum Research Fund administered by the American Chemical Society. A NATO travelling grant is also gratefully acknowledged.

REFERENCES

1. P. Rempp and E. Franta, *Adv. Polym. Sci.*, **58**, 1(1984).
2. P. Rempp, P. Lutz, P. Masson, P. Chaumont and E. Franta, *Makromol. Chem. Suppl.*, **13**, 47(1985).
3. K. S. Kazankii, P. Kubisa and S. Penczek, *Russ. Chem. Rev.*, **56**, 777(1987).
4. Y. Kawakami, in *Encyclopedia of Polymer Science and Engineering*, 2nd ed., H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges, Eds., J. Wiley, New York, **1987**, Vol. 9, p. 195.
5. V. Percec, C. Pugh, O. Nuyken and S. D. Pask, in *Comprehensive Polymer Science*, G. Allen and J. C. Bevington, Eds., Pergamon, Oxford, **1989**, Vol. 6, p. 281.
6. Y. Chujo and Y. Yamashita, in *Telechelic Polymers: Synthesis and Application*, E. J. Goethals, Ed., CRC, Boca Raton, **1989**, p. 163.
7. Y. Tsukahara, X. Jiang, N. Hayashi and Y. Yamashita, *Polym. J.*, **21**, 377(1989).
8. Y. Gnanou and P. Lutz, *Makromol. Chem.*, **190**, 577(1989).
9. S. Kobayashi, T. Mizutani and T. Saegusa, *Makromol. Chem.*, **185**, 441(1984).
10. S. Kobayashi, M. Kaku, S. Sawada and T. Saegusa, *Polym. Bull.*, **13**, 447(1985).
11. Y. Yamashita, Y. Tsukahara, K. Ito, K. Okada and Y. Tajima, *Polym. Bull.*, **5**, 335(1981).
12. Y. Yamashita, Y. Tsukahara, H. Ito, *Polym. Bull.*, **7**, 289(1982).
13. Y. Nagase, S. Mori, M. Egawa and K. Matsui, *Makromol. Chem., Rapid Commun.*, **11**, 185(1990).
14. T. Haide, C. Carre and A. Guyot, *Solid State Ionics*, **39**, 173(1990).
15. T. Duschek and H. A. Schneider, *Polym. Bull.*, **24**, 317(1990).
16. Y. Chujo, H. Kobayashi and Y. Yamashita, *Polym. Commun.*, **25**, 278(1984).
17. K. Mühlbach and V. Percec, *J. Polym. Sci., Part A: Polym. Chem.*, **25**, 2605(1987).
18. V. Percec and J. H. Wang, *J. Polym. Sci., Part A: Polym. Chem.*, **28**, 1059(1990).
19. V. Percec, U. Epple, J. H. Wang and H. A. Schneider, *Polym. Bull.*, **23**, 19(1990).
20. D. H. Solomon and G. Moad, *Makromol. Chem., Macromol. Symp.*, **10/11**, 109(1987).

21. D. Bednarek, G. Moad, E. Rizzardo and D. H. Solomon, *Macromolecules*, **21**, 1522(1988).
22. G. Moad and D. H. Solomon, in *Comprehensive Polymer Science*, G. Allen and J. C. Bevington, Eds., Pergamon, Oxford, **1989**, Vol. 3, p. 97.
23. D. H. Solomon, P. Cacioli and G. Moad, *Pure & Appl. Chem.*, **57**, 985(1989).
24. V. Percec and T. D. Shaffer, *J. Polym. Sci., Polym. Lett. Ed.*, **24**, 439(1986).
25. V. Jaacks, *Makromol. Chem.*, **161**, 161(1972).
26. G. Moad, E. Rizzardo, D. H. Solomon, S. R. Johns and R. I. Willing, *Makromol. Chem., Rapid Commun.*, **5**, 793(1984).
27. E. Rizzardo, A. K. Serelis and D. H. Solomon, *Aust. J. Chem.*, **35**, 2013(1982).
28. R. G. Griffiths, E. Rizzardo and D. H. Solomon, *J. Macromol. Sci., -Chem.*, **A17**, 45(1982).
29. J. C. Bevington, T. N. Huckerby and N. W. E. Hutton, *J. Polym. Sci., Polym. Chem. Ed.*, **20**, 2655(1982).