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Copolymerization behaviour of pentadiene-functional macromonomers obtained by free radical addition-fragmentation

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Abstract

Pentadiene-functional macromonomers based on poly (methyl methacrylate) (PMMA) and polystyrene (PS), obtained through a free radical addition-fragmentation reaction were copolymerized with styrene, methyl methacrylate (MMA) and methacrylic acid (MAA) to synthesise well defined graft copolymers. Thus, PMMA-g-PS, PS-g-PMMA and PS-g-PMAA of varying compositions and graft lengths were synthesised. The copolymerization kinetics revealed diminished reactivity of the pentadiene function of the macromonomer towards a given comonomer vis-à-vis the reactivities of the pentadiene monomer or the pentadiene function on the addition-fragmentation agent used to prepare the macromonomers. Methacrylic acid showed apparently reduced reactivity than MMA and the copolymerization of the former with PS-based macromonomer gave amphiphilic graft copolymers with different solubility characteristics. The reactivity of the terminal pentadiene-function of the macromonomer was found to be independent of its molar mass, although its reactivity was marginally diminished in comparison with pentadiene monomer. Low concentrations of high molar mass macromonomer led to the concomitant formation of homopolymers of the small monomer in the case of copolymerization with reactive monomers like MMA and MAA. The graft copolymers have been characterized by chemical methods and by GPC using multiple detectors.

Keywords: Free radical addition fragmentation; Macromonomers; Graft copolymer

1. Introduction

Graft copolymers with unique combination of the pendant and main chain have potential applications in the fields of surface coatings, blend compatibilizers, polymer alloys, surface active agents, surface modifiers, and emulsion stabilizers [1–4]. Among the vast variety of methods existing for the realization of graft copolymers, the macromonomer technique has been recognized as unique, since it leads to tailor-made polymers. A knowledge of the reaction kinetics can help predict the conditions for obtaining the desired copolymer. A large variety of macromonomers, encompassing different back bones and end-groups and their corresponding graft copolymers have been described [5–10]. The majority of macromonomers possess an acrylic or styrenic function, realized through chemical modification of the polymer chain terminal. Since such modification is carried out on the polymer, the efficiency of functionalization may not always be good. Free radical addition-fragmentation chain transfer has been recently identified as a method of preference for the single-step syntheses of macromonomers of vinyl polymers [10–16]. Almost all the reported addition-fragmentation agents give rise to terminal unsaturation that are α-substituted acrylic or styrenic groups. The polymerizability of such macromonomers is not good owing to secondary reactions [17]. Recently we have described a new addition-fragmentation agent, i.e. 5-*tert*-butyl thio penta-1,3 diene (TBTPD) with excellent chain transfer properties and capable of furnishing a pentadiene function at chain extremity [18,19]. Since free radical copolymerizability of pentadiene has been established [20–24], it was of interest to investigate the copolymerization of these pentadiene macromonomers so as to derive block copolymers. This article describes the copolymerization of these macromonomers with different comonomers. The kinetics of copolymerization and the characteristics of the graft copolymers have been reported.

2. Experimental

Methyl methacrylate (MMA), and styrene were purified by vacuum distillation. Methacrylic acid (MAA) was

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purified by passing through a neutral alumina column. The molar masses were estimated using gel permeation chromatography (GPC, Waters WISP710b automatic injector, Schimadzu LC6a pump, 4 PL-Gel columns coupled with Waters R401 refractometer, Beckmann 167 dual-UV detector and Chromatix CMX100 light scattering detector). NMR was recorded with a Bruker AC 200 MHZ spectrometer. DSC measurements were done on a Perkin-Elmer DSC-4 thermal analyzer.

2.1. Preparation of macromonomer

The macromonomers were prepared by polymerizing MMA or styrene in the presence of calculated amounts of TBTPD using a free radical initiator. The polymer was purified by repeated precipitation from its solution in tetrahydrofuran into a non solvent. Narrow molecular weight polymers were obtained either by limiting the monomer conversion to less than 20% or by fractionating the polymer prepared in high conversion. Details of the synthesis and characterization of macromonomer used in this study are given in a previous article [19] and the essential details given in Table 1.

2.2. Polymerization and purification of copolymers

The polymerization reactions were done in solution in Pyrex glass tubes (toluene or DMSO:dioxane mixture). Weighed amounts of the macromonomer, comonomer and initiator were dissolved in the solvent in the tube which was sealed under vacuum after deaeration. The polymerization was carried out in thermostated oil bath at the required temperature. After the polymerization, the contents were diluted with tetrahydrofuran (THF) to make approximately 5% solution and the copolymer was isolated by precipitation of the contents in selective solvents as detailed below. The solvents selected to solubilize the unreacted macromonomer were chosen through trial precipitation studies using pure macromonomers.

2.2.1. Purification of copolymers derived from polystyrene macromonomers

The precipitant used varied with molar mass of the macromonomer as given below.

Molar mass of macromonomer	Precipitant
up to 5000	Heptane:Cyclohexane, 5:1 (by volume)
5000–12 000	Heptane:Cyclohexane, 1:1
> 12 000	Cyclohexane

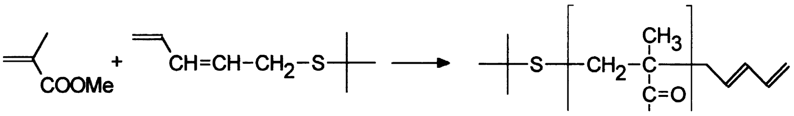
2.2.2. Purification of copolymers derived from PMMA macromonomers

The precipitant was methanol, containing 20% acetone up to a macromonomer molecular weight of 6500 and 40% acetone for macromonomers with molecular weights above that.

Table 1
Synthesis conditions and characteristics of macromonomers

Monomer and its quantity (mol)	Quantity of TBTPD[a] (mol)	Initiator and its quantity (mol)	Temperature of polymerization (°C)	M_n (GPC)	M_w/M_n	Remarks	Ref. of macromonomer
MMA, 0.47	0.022	AIBN, 0.0024	70	12770	1.63	All polymers obtained by fractionation of same batch of polymer formed in 42% yield	PM-12770
				6360	1.41		PM-6360
				2390	1.16		PM-2390
Styrene, 0.41	0.032	Ditert-butyl peroxide, 0.0027	135	12300	1.64	All polymers obtained by fractionation of same batch of polymer formed in 83% yield	PS-12300
				9170	1.41		PS-9170
				4840	1.32		PS-4840
				3970	1.20		PS-3970
Styrene, 0.25	0.0026	AIBN, 0.00037	70	19900	1.75	Conversion 13.6%	PS-19900
Styrene, 0.25	0.0016	AIBN, 0.00037	70	27400	1.91	Conversion 13.8%	PS-27400
Styrene, 0.43	0.021	Azobiscyanocyclohexane, 0.0020	105	48000	2.33	First fraction from polymer formed in 80% yield	PS-48000

[a] 5-*tert*-butyl thio penta-1,3 diene.



Scheme 1. Synthesis of pentadiene-functional macromonomer.

2.2.3. Purification of copolymers derived from polystyrene macromonomers and methacrylic acid

In this case the precipitant was cyclohexane and the solvent for redissolution of the copolymer was 1:1 DMSO:-dioxane mixture.

The precipitants were identified by precipitation trials using the macromonomers. The absence of dissolved copolymer in the precipitant was ensured from GPC as well as from NMR of the filtrate. In each case, the precipitant chosen is a poor solvent for the homopolymers of the comonomer. No attempt was made to remove the homopolymer of the comonomer, if any, in the system but its presence or absence was indicted from the GPC analyses of the isolated graft copolymer and are discussed in the text at relevant places. The isolated polymers were purified by reprecipitation using the same solvent–precipitant combination and were filtered, dried and weighed.

2.3. Characterization of copolymer

The copolymer composition was determined by elemental analysis or by NMR. Molecular weights were determined by GPC with multiple detectors.

3. Results and discussion

The syntheses of pentadiene-functional macromonomers were done by one-step synthesis (Scheme 1) using TBTPD as addition-fragmentation chain transfer agent in the radical polymerization of the required monomer [19]. As a result of the chain transfer, the polymer terminals are end-capped with a pentadiene moiety (see Scheme 1). Since the transfer constants are high the functionality of the formed polymers are also excellent. The macromonomers of both styrene and MMA used in this study possessed relatively narrow molar mass distribution. They were prepared either by low conversion polymerization or by fractionation of polymers prepared at high conversion as detailed elsewhere [19]. Their molar masses are given in Table 1. The functionality of these macromonomers could not be determined precisely by conventional methods due to interference of isolated unsaturation in the midst of the chain (whose polymerizabilty is negligible). Theoretical calculations lead us to expect them to possess greater than 95% functionality [19]. The *cis–trans* contents of the pentadiene terminal were also not precisely determined. A previous study on the copolymerization of *cis*- and *trans*-pentadiene with acrylonitrile revealed that they differ only slightly in their reactivities [20,21]. In that study, the predominant structure of the pentadiene moieties in the formed copolymer was identified as 1,4-*trans*, irrespective of the (*cis–trans*) nature of the pentadiene monomer. The formation of the graft copolymer is depicted in Scheme 2.

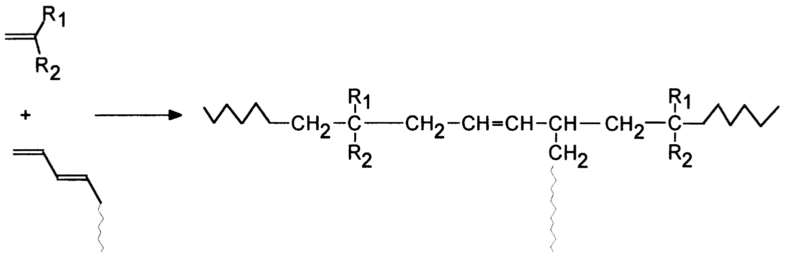
In the above scheme the copolymerization is depicted such that the reaction takes place mostly by 1,4- or 4,1-addition to the terminal pentadiene. The fraction of polymerization occurring through 1,2-, 2,1-, 3,4- or 4,3-additions has been found to be negligible in earlier studies on copolymerization of pentadiene [22–24]. It has also been found that the predominant structure of poly pentadiene is *trans*-1,4 [22]. In this work, the microstructure of the pentadiene in the copolymer was not of interest and hence not investigated.

3.1. Kinetics of copolymerization

In these cases, the structure and composition of the graft-copolymer depend upon the nature and composition of feed and the monomer reactivity ratios. The instantaneous copolymer composition in a binary copolymerization, following terminal model is given as

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]}=\frac{[\mathrm{M}_1]}{[\mathrm{M}_2]}\frac{(r_1[\mathrm{M}_1]+[\mathrm{M}_2])}{(r_2[\mathrm{M}_2]+[\mathrm{M}_1])}$$

When one of the monomers is a macromonomer (say M_1), its molar concentration can be neglected at all practical



Scheme 2. Synthesis of graft copolymers.

compositions and in this case, the expression for the copolymer composition is reduced to:

$$\frac{d[\mathrm{M}_1]}{d[\mathrm{M}_2]} = \frac{[\mathrm{M}_1]}{r_2[\mathrm{M}_2]}$$

or

$$r_2 = \frac{\dfrac{d[\mathrm{M}_2]}{[\mathrm{M}_2]}}{\dfrac{d[\mathrm{M}_1]}{[\mathrm{M}_1]}}$$

In this study, $[\mathrm{M}_1]$ represents the molar concentration of the macromonomer and $[\mathrm{M}_2]$ that of the comonomer (MMA, MAA or styrene). The reactivity ratio, r_2, of the small monomer (MMA, MAA or styrene) is therefore, the ratio of the proportion of its consumption to that of the macromonomer. In other words, the reactivity of the macromonomer is obtained as $1/r_2$. Thus, knowledge of r_2 is enough to predict the copolymer composition. If p_1 and p_2 are the fractional conversion of the macromonomer and comonomer respectively, then r_2 can be obtained by the integration of the above equation as:

$$r_2 = \ln(1 - p_2)/\ln(1 - p_1)$$

Determination of r_2 hence warrants precise determination of p_1 and p_2. In this study, r_2 was determined by the Jaack's single experiment technique through estimation of p_1 and p_2 [25]. This has been done by the quantitative isolation of the copolymers and determination of their composition by elemental analyses, after ensuring that the copolymer is devoid of the unreacted macromonomer.

3.2. Copolymerization of polystyrene macromonomers

3.2.1. Copolymerization with MMA (to form PMMA-g-PS)

The PS-based macromonomers of various molar masses (M_n) ranging from 2400 to 48 000 g/mol were used to copolymerize with MMA. The copolymerization conditions and copolymer characteristics are given in Table 2, Table 3. For purification of the copolymer, precipitation from THF into selective solvents was done as detailed above.

In each case, the filtrate was examined by GPC or NMR to ensure it did not contain dissolved copolymer. The conversions in respect of each monomer were estimated by quantitatively isolating the copolymer and by estimating their compositions from the carbon-content of the polymer. The homogeneity of the isolated polymer was checked from the GPC of the copolymer using different detectors. Since the backbone and the graft have different UV absorptivity, the superposability of the chromatograms with UV and refractive index detectors, especially in regions corresponding to the molar mass of the macromonomer, confirmed the absence of the residual macromonomer in the isolated copolymer. Typical GPC of the PMMA-g-PS can be found in Fig. 1.

Since the copolymers are branched, their molar masses calculated from GPC, using conventional detectors could be underestimated. Their molecular weights have been precisely determined by GPC using light scattering (LS) detector. As expected, the molar masses calculated by this technique were always superior to those determined by refractive index (RI)- or UV-detection. From the molar mass and the composition, the characteristics of the copolymer, such as the number of grafts per chain, sequence length between grafts, degree of polymerization, etc., were calculated. Examination of the results shows that the molar mass of the macromonomer has practically no effect on the reactivity ratio. This is in agreement with the general concept concerning the reactivity of macromonomers, i.e. that it is essentially chain length-independent. It may be noted that for macromonomers with medium molar mass, although the apparent reactivity was low for low concentrations of

Table 2
Copolymerization of MMA with low molecular weight PS-macromonomers in toluene at 70°C

Macro-monomer	Conc. of AIBN (mol/L × 10^2)	Conc. of MMA $[\mathrm{M}_2]$ (mol/L × 10^2)	Conc. of macro-monomer $[\mathrm{M}_1]$ (mol/L × 10^2)	Time of polymerization (min)	Global conversion (wt.%)	Wt.% of PS in copolymer	Conversion of MMA, p_2 (%)	Conversion of macromonomer, p_1 (%)	r_2	Molecular weight (GPC) × 10^{-3} (polydispersity index)			Average number of grafts per chain[a]	Degree of polymerization, D_p^a
										R.I.	U.V.	L.S.		
PS-3970	1.39	4.28	4.34	108	17.20	37.4	14.89	22.96	0.62	63.9 (1.88)	68.6 (2.04)	71.9 (1.34)	6.77	457
	1.26	3.88	5.89	110	14.26	47.4	11.81	18.31	0.62	56.5 (1.83)	56.4 (2.12)	73.0 (1.36)	8.71	392
	1.24	3.06	6.37	110	13.06	55.4	10.41	16.28	0.62	44.6 (1.80)	52.1 (1.81)	49.5 (1.35)	6.91	227
PS-12300	0.70	2.68	0.40	266	59.05	20.35	55.86	77.56	0.55	80.4 (2.13)	101.0 (1.86)	119.5 (2.12)	1.98	955
	0.70	2.68	1.07	266	51.10	43.24	43.29	67.02	0.51	112.7 (2.36)	117.1 (2.34)	163.1 (1.90)	5.73	920
	0.70	2.68	1.88	266	43.11	59.77	32.29	55.68	0.48	137.3 (3.04)	129.4 (3.09)	216.8 (2.52)	10.54	876

[a] Based on L.S.

Table 3
Copolymerization of MMA with high molecular weight PS-macromonomers in toluene at 70°C

Macromonomer	Polymerization time (min)	[AIBN] × 10^3 (mol/L)	[MMA] (mol/L)	$[M_1]$ × 10^2 (mol/L)	Global conversion (wt.%)	Wt.% of PS in copolymer	p_2 (%)	p_1 (%)	r_2	Molecular weight (GPC) × 10^{-3}		Average number of grafts per chain[a]
										R.I.	U.V.	
PS-19900	233	4.87	1.88	0.099	45.7	9.22	45.75	44.21	1.05	59.8 (2.1)	87.1 (1.6)	0.30
	233	4.87	1.88	0.15	48.3	14.45	47.80	50.69	0.92	56.1 (2.0)	74.0 (1.7)	0.40
	233	4.87	1.88	0.20	43.4	24.73	39.62	60.85	0.54	58.3 (2.1)	57.6 (2.2)	0.72
PS-27400	175	8.13	1.31	0.109	41.68	9.22	41.68	43.95	0.93	59.3 (2.0)	97.1 (1.6)	0.20
	175	8.13	1.31	0.178	40.86	14.15	40.06	42.82	0.92	61.1 (1.9)	90.2 (1.7)	0.31
	175	8.13	1.31	0.245	38.56	18.76	38.27	40.98	0.92	60.1 (2.0)	67.5 (2.2)	0.41
PS-48000	170	4.88	2.0	0.086	36.88	18.16	36.28	36.28	0.89	81.3 (2.5)	189 (1.9)	0.31
	170	4.88	2.0	0.13	34.10	23.00	33.05	33.05	1.04	89.1 (2.5)	176 (2.0)	0.40
	170	4.88	2.0	0.22	28.84	37.27	32.40	32.40	0.80	115 (2.6)	187 (2.1)	0.90

[a] Based on M_n by GPC using R.I.

macromonomer, it tended to increase with concentration, reaching the limiting value of 0.5 at relatively high macromonomer loading. This is due to the fact that at low macromonomer feed conditions, there could be formation of PMMA homopolymers and the purification technique employed here does not eliminate homo- or copolymer of MMA. Analysis of the resultant copolymers, by multi-detector GPC, did indicate the possibility of the presence of homopolymers (of MMA) when the macromonomer loading was low. As a result, the difference in molar mass and their distribution estimated by the UV- and RI-detectors was found to decrease as the macromonomer loading in the feed increased. This means that at low concentration of the high molar mass macromonomer, a significant proportion of the propagating chain terminates before encountering a macromonomer species, since in these cases the effective concentration of the pentadiene group is negligible. At significant concentration of the macromonomer, the copolymer is devoid of the homopolymer of MMA and consequently, the experimentally determined reactivity ratio approaches the limiting value. Further, the GPC patterns using the two detectors (RI and UV) tend to be identical, as are the molar masses.

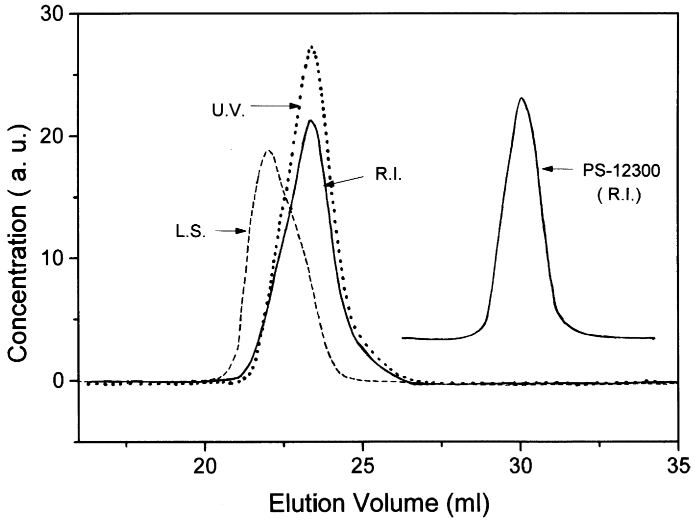


Fig. 1. GPC diagrams of PMMA-g-PS with different detectors and that of the macromonomer, PS-12300 used for its synthesis. Extent of styrene grafting: 53.42%.

For polymerization systems containing macromonomers of very high molar mass ($> 27\,000$) the apparent reactivity of the macromonomer, as calculated from the r_2 value is low for the reasons stated above for all the compositions studied. The significant differences of the isolated copolymers in their molar masses and the GPC pattern (by UV and RI detectors) are indicative of the contamination of the graft copolymers with homopolymers of MMA. Probably at very high concentrations of the macromonomers, the reactivity ratio might tend to the limiting value, but such systems could not be studied here owing to the difficulty in quantitative isolation of the copolymers, which tended to be emulsified in the precipitant.

Percec et al. have noted similar apparent concentration dependency of the macromonomer reactivity and have attributed the observation to the better solvation of the macromonomer chain terminal in dilute solution, which increases the excluded volume effect, thus making the intertwining of the propagating chains difficult [26–28]. But it appears to us that the authors have probably overseen the possibility of experimental error in determining the reactivity ratios, arising from the presence of homopolymers at low macromonomer concentration.

The reactivity ratio calculated in the case of macromonomer-MMA ($r_2 = 0.6$–0.5) is more than that determined from the transfer constant ($r_2 = 0.34$) of the TBTPD for MMA [19]. This shows that the pentadiene function in macromonomers is less reactive than that in the chain transfer agent. However, this value is closer to the reactivity ratio reported for the pair pentadiene (M_1)–MMA [21] ($r_2 = 0.40$).

It can be seen that, at fixed concentrations of monomer and initiator, the apparent copolymerization rate and polymer molar masses decrease drastically as the macromonomer loading in the feed increases. This behaviour is typical of the copolymerization of MMA with pentadiene where the reduced propensity of the stable pentadiene radical to react with the electron-deficient MMA monomer causes a decrease in propagation rate. Added to this, the enhanced cross termination could also reduce the molecular weight. Similar behaviour has been observed in a MMA–pentadiene system in a separate study [29]. The variations in polymerization rate and molecular weight of the copolymer system with concentration of the macromonomer are shown in Fig. 2.

3.2.2. Copolymerization with methacrylic acid

Amphiphilic copolymers based on polymethacrylic acid, bearing uniform polystyrene grafts prepared by the macromonomer technique have recently been reported [30]. Such polymers show water absorption and emulsifying properties. Blends of these polymers with other amphiphilic copolymers have potentiality to serve as chemical valves. Pentadiene macromonomers were also copolymerized to synthesize similar copolymers. Here, a PS-based macromonomer was copolymerized with methacrylic acid. The polymerizations were performed in a DMSO:dioxane mixture in which the system was completely homogeneous. Purification of copolymers was done by repeated precipitation in cyclohexane which dissolved out the unreacted macromonomer. Details regarding the polymerization conditions can be found in Table 4. The calculated reactivity ratio was found to vary with composition. The apparent reactivity ratio (r_2) is lower at low concentration of the macromonomer, and on increasing its concentration, the values tend to reach that of MMA. This is a consequence of the contamination of the isolated graft copolymer with the homopolymer of MAA at lower concentrations of the macromonomer. The copolymers, containing small quantities of styrene (10%), were found to swell in dilute NaOH solution and those rich in styrene dissolved in DMSO–THF (or chloroform) mixtures. When the reaction was carried out in a

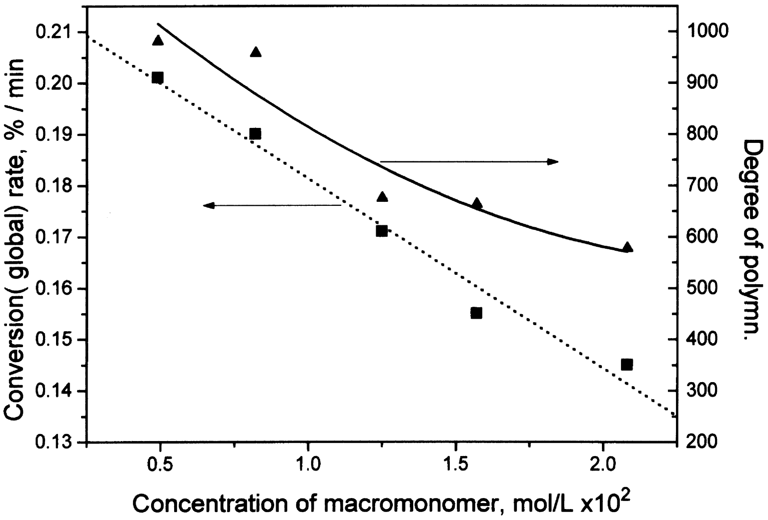


Fig. 2. Variation of apparent copolymerization rate and copolymer molar mass with feed composition at constant monomer and initiator concentration for the polymerization of MMA with macromonomer, PS-9100.

Table 4
Copolymerization of methacrylic acid (MMA) with macromonomer, PS-4840 in DMSO–dioxane mixture, [MMA] = 2.32 mol/L, [AIBN] = 4.88×10^{-3} mol/L, temperature = 70°C, time = 215 min

Conc. of macromonomer, $[M_1]$ (mol/L × 10^2)	Global conversion (wt.%)	Wt.% of PS in copolymer	Conversion of MAA, p_2 (%)	Conversion of macromonomer, p_1 (%)	r_2
0.81	69.1	8.70	75.3	36.50	3.00
1.64	43.1	23.21	46.1	35.20	1.43
2.42	34.7	30.80	40.0	28.90	1.40
2.77	38.9	49.60	32.7	48.00	0.60

precipitating medium like dioxane, a substantial amount of PMAA was found to form even at high macromonomer concentrations.

3.3. Copolymerization of PMMA-macromonomers with styrene

PMMA-based macromonomers of varying molar masses were copolymerized with styrene and the details can be found in Table 5. In this case, the studies were limited to macromonomers of relatively lower molar mass. The copolymer was purified by precipitation into methanol containing 20–40% (by volume) of acetone which dissolved out the unreacted macromonomer. In this case also the absence of graft copolymer in the precipitant was verified by GPC analysis using a UV detector. The homopolymer of styrene, if any, was not removed. However, its absence was ascertained from GPC analysis, where the superposability of the chromatograms obtained with UV and RI detectors indicate the compositional homogeneity of the isolated copolymers.

The calculated reactivity ratios, r_2, did not generally show much dependency either on macromonomer concentration or on its molar mass. The majority of the values converge at $r_2 = 2.4$. This value shows that the pentadiene in the macromonomer is less reactive (towards styrene) than that present in the precursor chain transfer agent (whose $r_2 = 1$). It is also less reactive than the pentadiene monomer, where the reactivity ratio, r_2, for the pair pentadiene (M_1)–styrene (M_2) has been reported as 1.23 [23]. Owing to the diminished reactivity of the macromonomer towards styrene, the copolymers carried fewer grafts. The molar masses of PS-g-PMMA polymers were generally inferior to those of PMMA-g-PS, due to the reduced propagation rates (both homo-propagation and cross-propagation) of the two electron-rich monomers (i.e. styrene and pentadiene). Since the comonomer in this case (i.e. styrene) is less reactive than the methacrylates, the copolymers were devoid of contamination by the homopolymer of it. The molar masses in these cases, determined by GPC using RI and UV detectors, can be considered as practically absolute since, error caused by chain branching is not significant. The apparent copolymerization rate and the molar mass (D_p) showed only a slight decrease with increase in macromonomer concentration in the feed. This arises from the fact that, although the styryl radical has a reduced tendency to react with

Table 5
Copolymerization of styrene (M_2) with PMMA-macromonomers (M_1) at 70°C in toluene

Macromonomer	Polymerization time (min)	$[M_2]$ (mol/L)	[AIBN] × 10^3 (mol/L)	$[M_1]$ × 10^2 (mol/L)	Global conversion (wt.%)	Wt.% of PMMA in copolymer	p_2 (%)	p_1 (%)	r_2	M_n (GPC) × 10^{-3} (M_w/M_n)		D_p	Average number of grafts per chain[a]
										R.I.	U.V.		
PM-2390	120	2.90	10.2	1.46	10.00	4.18	11.35	4.27	2.76	27.7 (1.91)	24.9 (1.92)	255	0.50
	120	2.90	10.2	2.01	10.28	5.60	11.24	4.19	2.78	30.9 (1.80)	25.8 (2.02)	279	0.75
	120	2.90	10.2	2.72	10.00	7.40	11.25	4.17	2.79	28.8 (1.80)	25.1 (1.98)	254	1.0
PM-6360	174	1.74	6.10	2.13	7.55	22.74	10.20	4.01	2.63	19.1 (1.62)	17.2 (1.68)	142	0.68
	174	1.74	6.10	2.79	7.21	30.41	9.94	4.43	2.31	20.3 (1.62)	18.2 (1.71)	134	1.0
PM-12770	174	1.70	6.10	0.86	8.76	21.08	11.10	4.90	2.34	30.3 (1.89)	25.4 (2.10)	230	0.50
	174	1.70	6.10	1.02	8.88	25.29	11.39	5.38	2.20	29.8 (1.97)	26.7 (2.11)	213	0.60
	174	1.70	6.10	1.33	8.11	36.55	11.00	5.05	2.25	32.1 (2.03)	28.9 (2.07)	197	0.92

[a] Based on M_n by GPC using R.I.

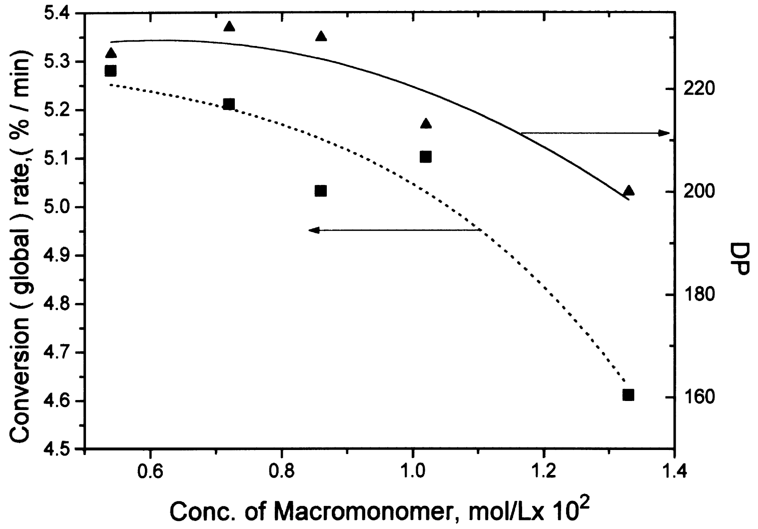


Fig. 3. Variation of apparent copolymerization rate and copolymer molar mass with feed composition at constant monomer and initiator concentration for the polymerization of styrene with the macromonomer, PM-12770.

pentadiene (evident from the high r_2 value), it is compensated by the enhanced reactivity of the resulting pentadiene radical towards the radicophilic styrene. The result is that the global propagation rate and hence the molar mass remain practically unaltered. The slight decrease in D_p must be a consequence of the enhanced rate of cross termination (Table 5). The trends in polymerization rate and molecular weight with macromonomer concentration is shown in a typical case in Fig. 3.

3.4. Physical characteristics of copolymers

It is known that block and graft copolymers tend to have micro phase separation of their segments when the segments are sufficiently long. A similar behaviour was exhibited by these graft copolymers as well. During the synthesis of copolymers using high concentration of macromonomer of molar mass above 18 000, as the polymerization advanced, the polymerization medium became turbid due to clear phase segregation. DSC analyses of the isolated copolymer showed only a single T_g for the PMMA-g-PS polymers when the PS sequence did not exceed 4000 g/mol. Fig. 4 shows the DSC thermograms for typical copolymers of short and long grafts. Two distinct T_g values, as a consequence of phase separation, can be seen in the latter case where each phase embeds the other to a certain extent. Copolymers with graft length around 4000 showed glass

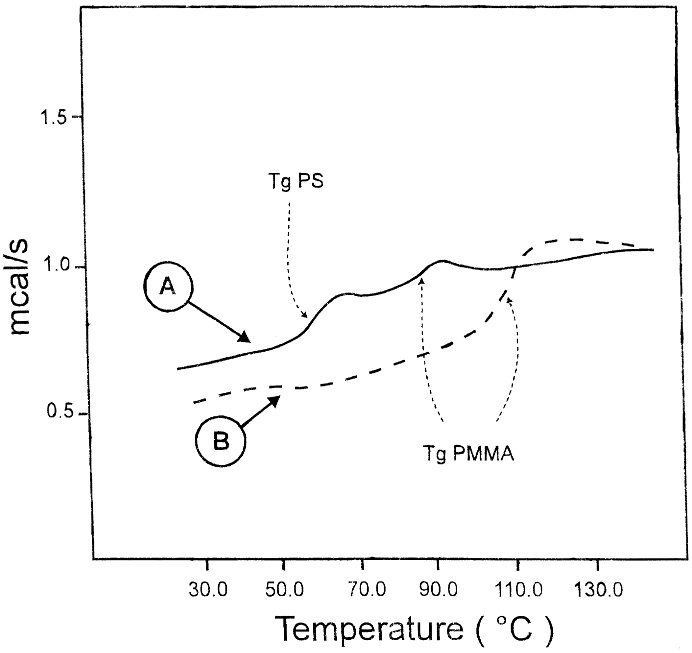


Fig. 4. DSC analyses of some PMMA-g-PS copolymers: (A) molecular weight of PS sequence 3970, extent of grafting 56%; (B) molecular weight of PS sequence 9100, extent of grafting 54%.

transition in a wide range (70–110°C), indicating that at this threshold chain length, the phase is not perfectly homogeneous, and is on the verge of separation.

4. Conclusions

The copolymerizability of pentadiene-functional macromonomer obtained by a single-step free radical addition-fragmentation reaction has been demonstrated. In the present study, it has been found to copolymerize with both electron-rich and electron-deficient comonomers in conformation with the theoretical reactivities. The reactivity is more towards electron-deficient monomers such as methyl methacrylate and methacrylic acid than to an electron-rich one such as styrene. Copolymerization with methacrylic acid is a means to obtain amphiphilic graft copolymer. The reactivity of the terminal pentadiene is quite independent of the molar mass of the macromonomer bearing it. Its reactivity is, however, moderately less than that of the TBTPD, the precursor used to generate the macromonomer and the pentadiene itself. At low molar concentrations of the macromonomer, the copolymer formed is contaminated with some homopolymer of the comonomer and in this case, additional purification steps are warranted to derive pure graft copolymer. Knowledge of the kinetic parameters is helpful in pre-determining the reaction parameters for obtaining tailor-made graft copolymers. The invariance in the reactivity of the terminal functions with molar mass of the macromonomer is an added advantage. The present pentadiene-functional macromonomer system is more suited to copolymerization with electron-deficient monomers such as acrylates.

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