Synthesis of Graft Copolymers. Part I. Synthesis of Macroinitiators

GRACIELA MORALES, EFRAÍN CASTRO, ELENA KALUYZHNAYA, and RAMIRO GUERRERO-SANTOS*

Centro de Investigación en Química Aplicada, Blvd. Enrique Reyna Hermosillo, 140, Apdo. Postal 379, Saltillo, Coahuila, Mexico

SYNOPSIS

Thermal polymeric initiators, having pendant 1,2-bis(trimethylsilyloxy)tetraphenylethane (or benzopinacolate) groups along the chain, have been prepared. First, the reactivity ratios of 4-vinylbenzophenone (4VBP) and 4-methacryloyloxybenzophenone (MOB) copolymers with styrene or methylmethacrylate were determined. Then the randomly containing 4VBP or MOB copolymers were transformed into polymeric initiators by duplication reaction of the attached benzophenone. Polymerization of MMA or St initiated by the resulting copolymers having pendant benzopinacolate groups was carried out yielding PMMA-*g*-PS and PS-*g*-PMMA. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The 1,2-bis(trialkylsilyloxy)tetraphenylethane or benzopinacolate groups represent a relatively new class of free radical thermal initiators. Benzopinacolates were first prepared by Calas[1] and tested as initiators in free radical polymerization of styrene and methylmethacrylate at temperatures between 80 and 110°C by Braun.[2] At these temperatures, the C—C bond easily cleaves, yielding an unusually high concentration of hemibenzopinacolate radicals, which are relatively stable due to a resonance effect.[3] Then these C—C bond-splitting initiators were used for the synthesis of block copolymers through a macroinitiator technique. For instance, vinyl functional benzopinacolate was attached to α,ω-hydrogen functional poly(dimethylsiloxane), and the resulting polymer was used as a free radical initiator for styrene to get the (PS-*b*-PDMS)n multiblock copolymer.[4] A similar approach was used in order to get PEO-*b*-PS.[5] Because of the stability of hemibenzopinacolate radicals the rate of initiation is low, and primary termination of initiated chains takes place producing end-terminated hemibenzopinacolate oligomers. However, the most important feature of this polymerization is the increasing of the molecular weight of the polymer in time. It is believed that the formed oligomers grow by further insertion of molecules of the monomer between the last monomer unit and the hemibenzopinacolate group. This mechanism was proposed by Otsu to explain the increase of molecular weight with the conversion in polymerizations initiated by tetraalkyl thiuram disulfides and tetraphenylethanes.[6] Although this mechanism reasonably explains the experimental facts, model molecules representing the supposed active extremity have been recently found to be unable to initiate polymerization in the case of styrene polymerization initiated with benzopinacolate.[7] This result points out the necessity for new experiments in order to verify the mechanism of the increase of molecular weight with the conversion or "living character" in free radical polymerization initiated by benzopinacolate. In this article, we describe the synthesis of stable poly(styrene) or poly(methylmethacrylate) free radical initiators, randomly containing pendant 1,2-bis(trimethylsilyloxi)tetraphenylethane groups. They represent a new class of macroinitiators with living character that is able to initiate graft polymerization with high efficiency.

EXPERIMENTAL

Tetrahydrofuran (THF) was distilled over a sodium–benzophenone complex and used immediately.

* To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 57, 997–1004 (1995)
 CCC 0021-8995/95/080997-08

Benzonitrile, chlorotrimethylsilane, and hexamethylphosphoramide (HMPA) were purified by fractionate distillation; benzophenone was recrystallized from ethanol. The 2,2′-azobis-2-methylpropionitrile (AIBN) was recrystallized twice from methanol. 4-Hydroxybenzophenone, triethylamine, and methacryloylchloride were used as received. Monomers were distilled over sodium. Except AIBN (Pfaltz & Bauer Inc.), all reactives were from Aldrich Co.

NMR spectra were obtained with a Varian 200-MHz spectrometer. Mass spectra were recorded on a GC/MSD HP 5971 A. UV spectra were taken on a UV/Vis spectrometer HP 1050. SEC analysis was made in THF on a Waters 150 LC with polystyrene standards and monitoring refractometrically. Elemental analysis was performed by Galbraith Laboratories Inc.

Synthesis of 4-Vinylbenzophenone (4VBP)

4-Vinylbenzophenone was prepared by the reaction of 4-ethenylphenyl-magnesium chloride with benzonitrile in dry THF. The crude monomer was purified first by column chromatography with silica gel as a stationary phase and benzene as an eluent, then by crystallization from methanol giving yellow crystals (yield 55%). ^{1}H NMR spectrum ($CDCl_3$, ppm): 5.4 d(J = 10.8 Hz), 1H; 5.9 d(J = 17.1 Hz), 1H; 6.8 dd(J_{cis} = 10.8 Hz, J_{trans} = 17.1 Hz), 1H; 7.5–7.8 m, 9H. GC/MS analysis showed a pure compound in gas chromatography. Mass spectrum (m/e) 208 (M+), 131, 105, 77.

Synthesis of 4-Methacryloyloxybenzophenone (MOB)

Equimolar amounts of 4-hydroxybenzophenone, methacryloyl chloride, and triethylamine were reacted in dry acetone at 5°C for 5 h. The triethylamine hydrochloride was removed by filtration and the product was purified by column chromatography using silica gel as a stationary phase and benzene as an eluent. Yield 88%. ^{1}H NMR spectrum ($CDCl_3$, ppm): 2.1, s, 3H; 5.8, s, 1H; 6.4, s, 1H; 7.2–8.0, m, 9H. GC/MS analysis showed a pure compound. Mass spectrum (m/e) 266 (+), 169, 141, 121, 105, 69, 51.

Reactivity Ratios for Benzophenone-Containing Monomers with Methylmethacrylate (MMA) and Styrene (St)

Bulk radical polymerization of 4VBP–MMA, 4VBP–St, MOB–MMA, and MOB–St pairs was carried out in sealed evacuated Pyrex glass tubes at 60°C in the presence of AIBN at different molar ratios. The tubes were deoxygenated by three cycles of freezing, evacuating, and thawing, and were sealed off at the pressure of 1 torr. After reaction and dilution with THF, the copolymers were precipitated twice from methanol. The conversions were limited to less than 10%. The monomer content in the copolymers was determined by elemental analysis or ^{1}H NMR. Monomer reactivity ratios were calculated by Fineman–Ross[8] and Mayo–Lewis[9] methods. Values for r_1 and r_2 are presented in Table I.

Synthesis of PS and PMMA-Based Macroinitiators by the Reductive Duplication Reaction of Benzophenone Pendant Groups

The synthesis of polymeric initiators was carried out according to the procedure described by Calas[1] for the preparation of benzopinacolates, but in the presence of 4VBP- or MOB-containing copolymers. A typical experiment was as following: 6 g of poly(4VBP-*co*-MMA) (containing 7.4 mol % of 4VBP and M_n = 30,000), 0.1 mol of benzophenone, 0.1 mol of chlorotrimethylsilane, 50 mL of dry THF, and 0.05 mol of Mg powder were placed into a flask under argon atmosphere. HMPA (5 mL) was added to start the reaction. The temperature quickly raised to 50–60°C, and after 30 min decreased to room temperature. The stirring was continued overnight and the resulting polymer was isolated from organic and inorganic products by filtration and subsequent precipitation from ethanol as many times as necessary to obtain a pure product. In a similar way, polystyrene-based macroinitiators were prepared. Polymeric initiators were also prepared from MOB–St and MOB–MMA copolymers. Conversion of fixed benzophenone was determined by UV spectroscopy and the molecular weight by SEC.

Table I Reactivity Ratios of 4VBP and MOB with St and MMA

Pair	Finemann-Ross		Mayo-Lewis	
M1-M2	r_1	r_2	r_1	r_2
4VBP-ST[a]	2.69	0.64	2.45	0.48
4VBP-MMA	1.94	0.29	2.17	0.31
MOB-St	0.33	0.33	0.26	0.28
MOB-MMA	1.66	0.73	1.78	0.69

[a] The monomer reactivity ratios were found r_1 = 3.0 and r_2 = 0.18 in ref. 10.

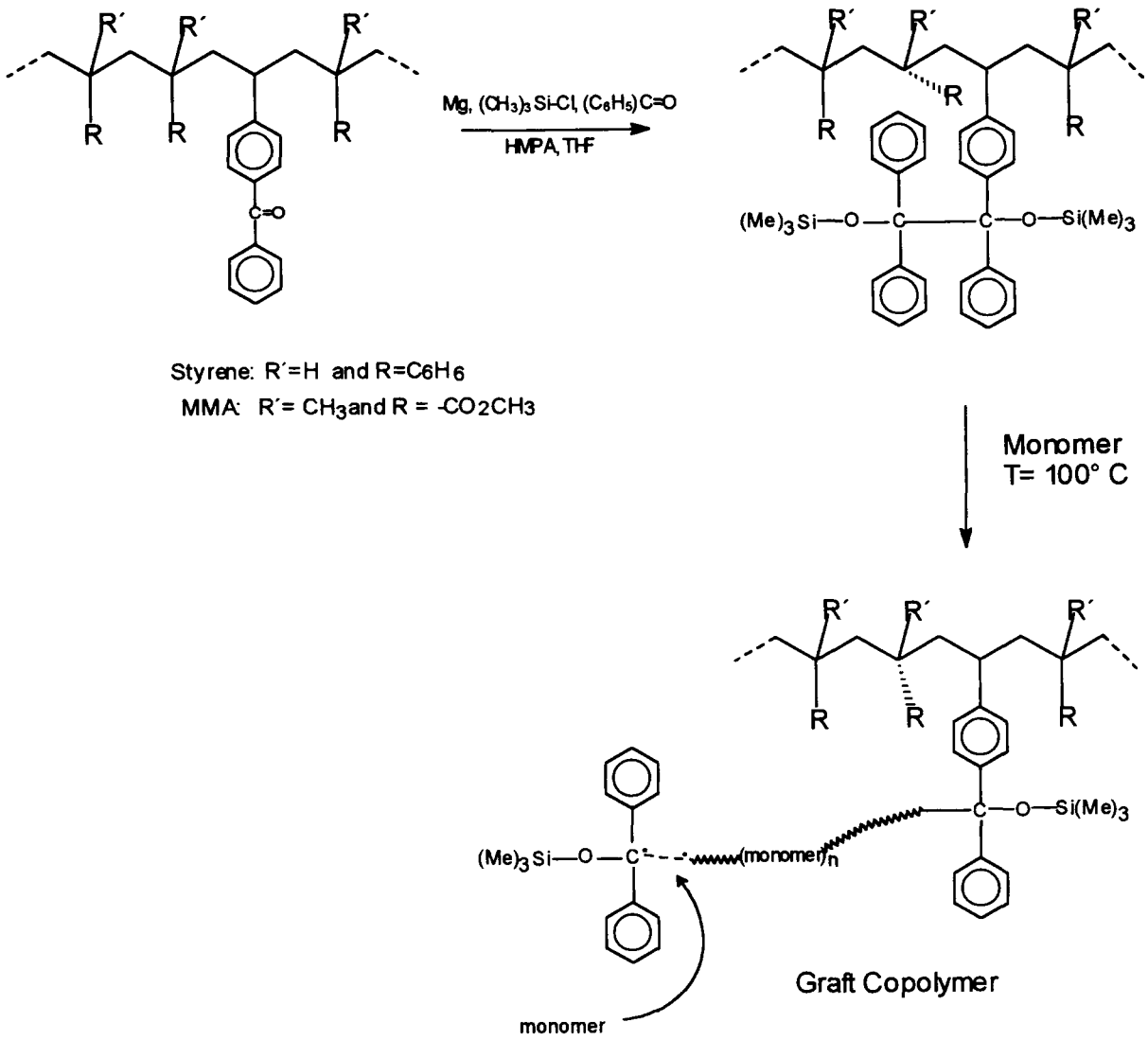

Figure 1 Synthesis of graft copolymers through benzopinacolate-based macroinitiators.

Synthesis of Poly(styrene-*g*-methylmethacrylate) and Poly(methylmethacrylate-*g*-styrene)

Graft polymerization of different monomers initiated with MMA- or St-based macroinitiators was carried out as following: the macroinitiator was dissolved in styrene (or MMA) monomer, and equal amounts of the resulting solution were placed into six glass tubes. The cooled tubes were evacuated, sealed, and kept at 90–100°C for 15, 30, 60, 90, 120, and 180 min. Conversion of pure thermal polymerization of St and MMA was measured under the same conditions. The polymers were isolated by precipitation from a large excess of methanol. After filtration, they were dried in vacuum at 50°C to a constant weight. The molecular weight relative to linear polystyrene was determined by SEC. In the case of the PMMA initiator, obtained polymers were extracted with acetonitrile to eliminate not-reacted macroinitiator and then with cyclohexane to eliminate poly(styrene) eventually formed. The same solvents were used to purify graft copolymers obtained with PS-based macroinitiator.

RESULTS AND DISCUSSION

Synthesis of Copolymers with 4VBP and MOB

Chemical modification of copolymers containing benzophenone groups for the case of 4-vinylbenzophenone copolymers is presented in Figure 1. Thermal cleavage of the resulting benzopinacolate groups produces the hemibenzopinacolate free radicals that are able to initiate polymerization of vinyl monomers yielding graft copolymers. From this figure it can be

Table II Experimental Details of Synthesis and Characteristics of Random Copolymer Used for the Synthesis of Macroinitiators

Copolymer	T (°C)	[AIBN] (M/L)	[M1]/[M2]	Yield (%)	w/w % Monomer Containing Benzophenone	$M_n \times 10^{-3}$
N° M1-*co*-M2						
1. 4VBP-*co*-St	60	0.11	0.06	51.8	16.5[a]	10
2. 4VBP-*co*-St	60	0.11	0.03	68.3	4.3[b]	10
3. 4VBP-*co*-MMA	60	0.12	0.06	32.6	24.0[b]	59
4. 4VBP-*co*-MMA	60	0.11	0.03	31.5	14.0[b]	70
5. 4MB-*co*-St	60	0.11	0.06	65.7	17.9[a]	11
6. 4MB-*co*-St	60	0.11	0.03	66.3	9.9[a]	11
7. 4MB-*co*-MMA	60	0.11	0.06	46.4	21.4[b]	119
8. 4MB-*co*-MM	60	0.11	0.03	32.6	6.1[b]	115
9. 4-VBP-*co*-St	60	0.11	0.05	92.0	12.5[a]	25.5
10. 4VBP-*co*-MMA	60	0.12	0.04	31.0	15.0[b]	27.4

[a] Calculated from the content of oxygen determined by elemental analysis.
[b] Calculated from ^{1}H NMR spectra.

seen that the number and relative position of these modifiable benzophenone units determine the structure and, therefore, final properties of graft copolymers. Thus, for a better understanding of the mode of the distribution of benzophenone-containing monomer we determined reactivity ratios by the methods of Finemann–Ross and Mayo–Lewis. The monomer reactivity ratios calculated by these two methods are in a good agreement (see Table I).

Examination of the values of Table I allows us to know the relative facility of benzophenone-containing monomers to incorporate in copolymers. In the case of pairs 4VBP–St and MOB–MMA, the r_1 r_2 product is close to unity, indicating random addition of monomers in the copolymer. For the pair MOB–St, $r_1 = r_2 = 0.33$, which reveals azeotropic properties and some tendency toward alternation. These values confirm that benzopinacolate groups formed from benzophenone will be rather distributed in aleatory form for all cases except for the MOB–St pair where a certain degree of regularity could be expected.

For the synthesis of macroinitiators, random copolymers were obtained, having low molecular weight and the content of the monomer containing benzophenone less than 24 wt %. Such values of these parameters were chosen bearing in mind that dissolution of the polymers for the modification and for the synthesis of graft copolymers will be difficult for high values of molecular weight. Besides, the limitation of the molecular weight reduces the average number of modifiable sites in the chain. High values of this parameter increase the risk of network formation in the graft polymerization with multifunctional initiators. Thus, the monomers 4-VBP and MOB were both copolymerized with styrene and methylmethacrylate, and a series of copolymers with different contents of 4-VBP or MOB was prepared and subsequently transformed into macroinitiators. The experimental conditions and results of these copolymerizations are given in Table II.

Synthesis of Poly(styrene)- and Poly(methylmethacrylate)-Based Polymeric Initiators

The synthesis of macroinitiators was made in the conditions of benzophenone duplication as described in Figure 1. In order to avoid reactions between benzophenone groups in the same polymeric chain or between benzophenone groups belonging to different chains, we used a 10-fold excess of free benzophenone with respect to attached benzophenone. After isolation from organic and inorganic products, it was confirmed by thin layer chromatography that macroinitiators did not contain any residual benzophenone or free benzopinacolate. The molecular weight (M_n) of the macroinitiators was determined by SEC. It was found that the M_n of styrene copolymers did not change, while the M_n of copolymers with methylmethacrylate drastically decreased (see Table III). This effect is probably produced by the rupture of methylacrylate copolymers during formation of macroinitiators, which involves the formation of hemibenzopinacolate free radicals in high concentration. Also, side reactions like chain transfer and coupling of methylacrylate copolymers, for example, poly(4MB-*co*-MMA), produce crosslink-

Table III Characteristics of Macroinitiators Synthesized According with Figure 1

No.	Copolymer Precursor (% Bz)	% Benzopinacolate Based on %Si (w/w)	F	$M_n \times 10^{-3}$	Benzophenone Conversion (%)[a]
1i.	4VBP-*co*-St(13.7)	8.9	2.48	11	27.6
2i.	4VBP-*co*-St(4.3)	5.8	1.41	11	21.3
3i.	4VBP-*co*-MMA(24)	23.9	7.11	30	54.0
4i.	4VBP-*co*-MMA(14)	16.5	3.69	30	50.9
5i.	4MB-*co*-St(19.7)	17.7	4.30	13	54.5
6i.	4MB-*co*-St(2.9)	10.0	1.88	10	45.5
7i.	4MB-*co*-MMA(21.4)	19.6	> 4.64	10	> 50.0
8i.	4MB-*co*-MMA(6.1)	16.9	1.63	17	68.8
9i.	4VBP-*co*-St(12.5)		3.96	20	60.0
10i.	4VBP-*co*-MMA(18.9)		3.82	32	

F = number of benzopinacolate sites by 100 monomer units.
[a] Conversion of bonded benzophenone was calculated from UV spectra.

ing of a small amount (in some cases up to 10%) of macroinitiators.

The UV spectra of macroinitiators allow us to determine the yield of the reaction of the benzopinacolization, which was, in all cases, close to those previously reported for benzophenone.[1] From the content of Si determined by the elemental analysis, the percent of benzopinacolate was calculated and, thus, the average number of reactive sites by each 100 monomer units in the macroinitiator chain was determined. These data are shown in Table III. The values obtained in such a way are, however, higher than the values calculated from conversion of benzophenone in the case of copolymers composed only of methacrylate monomers. This result can be explained by transformation, to some extent, of the carbonyl group of methacrylate monomers.

The transformation of benzophenone groups into benzopinacolates was also confirmed by the method of NMR spectroscopy. Thus, the decrease of the intensity of the peaks between 7.4 and 7.9 ppm (aromatic protons adjacent to carbonyl groups in benzophenone fragments) and the appearance of a large peak at −0.1 pmm (protons of trimethylsilyl groups) in ^{1}H NMR spectra of initiators after the reactions of transformation can be observed (see Fig. 2).

Synthesis of Graft Copolymers

In order to verify activity of macroinitiators, some of those reported in Table III were used for the synthesis of graft copolymers. Polystyrene-based macroinitiators, for example, 9i, were used to initiate graft copolymerization of methylmethacrylate, and the poly(methylmethacrylate)-based macroinitiators (10i) were used to prepare PMMA-*g*-PS. After polymerization, homopoly(methylmethacrylate) was eliminated by precipitation with acetonitrile, and polystyrene was extracted with cyclohexane. Figure 3 shows the conversion curves for the polymerization of styrene initiated by the PMMA-initiator and purely thermal polymerization for styrene under the same conditions. The data for the polymerization of the MMA monomer initiated by 9i are presented in Figure 4. The content of insoluble graft copolymer is also quoted. From these figures we can clearly see that the increase of the conversion cannot be attributed to the thermal polymerization, which does not exceed 4% after 180 min in both cases. Because macroinitiators do not contain any free benzopinacolate, the only source of free radicals are the benzopinacolates bonded to the chain.

From the Table IV, we can see that graft copolymers can be obtained with high efficiency, but the multifunctionality (4 benzopinacolate groups each 100 monomeric units of polymeric initiator) of polymeric initiators and the conditions of bulk copolymerization produce considerable amounts of crosslinked graft copolymer. About 20% of polymeric initiator 10i was inactive, and production of homopoly(styrene) increased with time. In the case of poly(styrene) initiator 9i, pure soluble copolymers were analyzed by ^{1}H NMR in order to determine their composition, which was found to be 54, 50, 14, 7, and 5 wt % of PS for 15, 60, 90, 120, and 180 min, respectively.

In according with the living radical polymerization mechanism,[6] the end of the growing chain in polymerization initiated with benzopinacolates is associated with the hemibenzopinacolate radical and the molecular weight increases through insertion of the monomer between the last monomer unit of the

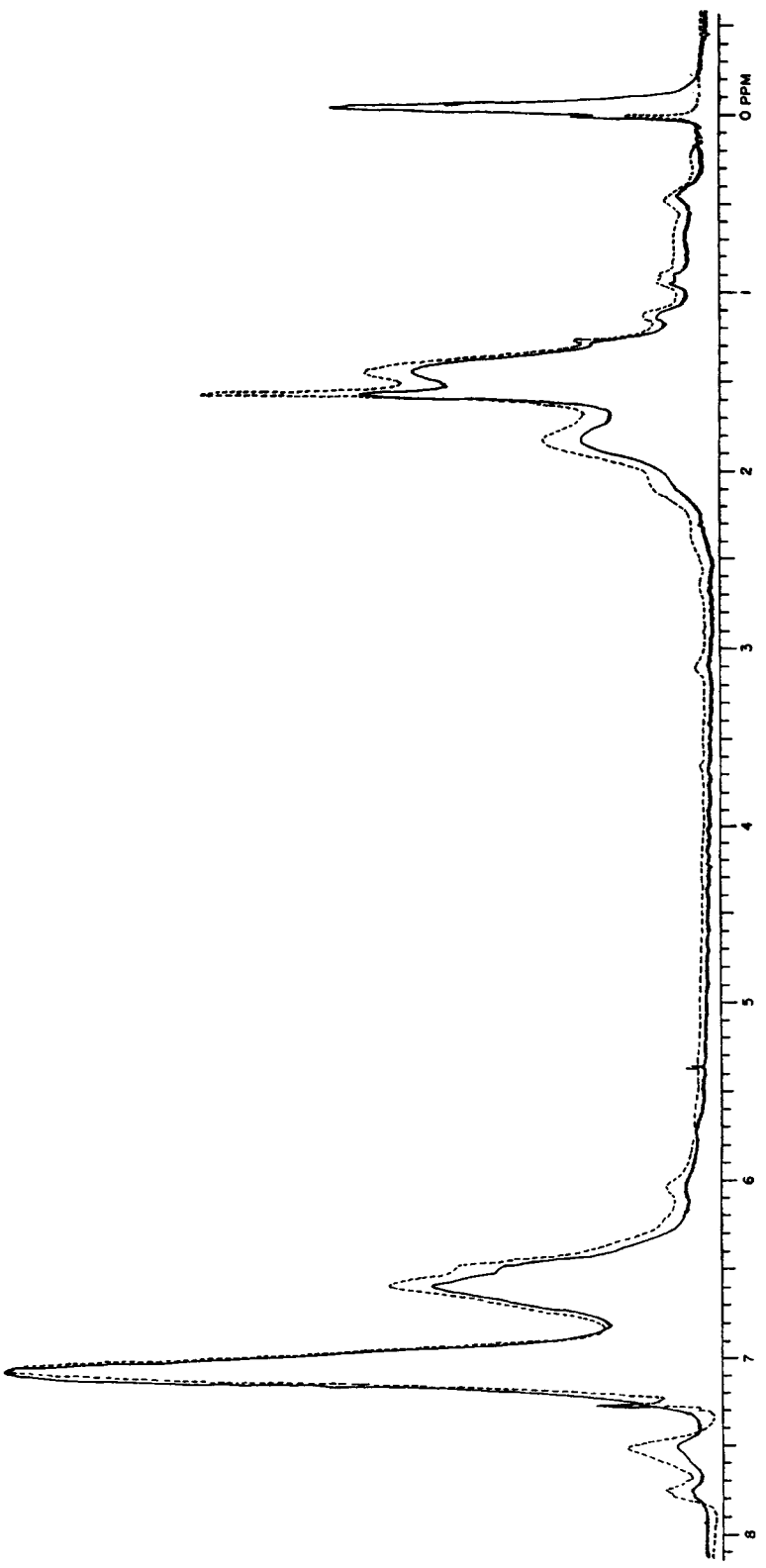

Figure 2 ^{1}H NMR (CDCl) spectra for the poly(St-*co*-4VBP) containing 18% in weight of 4-vinylbenzophenone before (---) and after transformation (—).

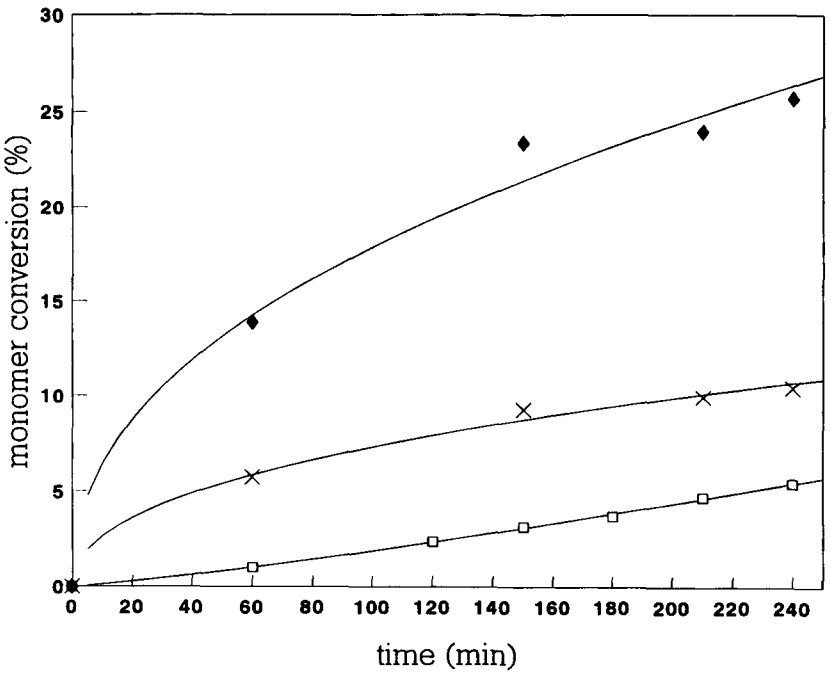

Figure 3 Conversion vs. time for bulk polymerization of styrene initiated with poly(methylmethacrylate) initiator 10i (♦), content of crosslinking copolymer (×), and thermal poly(styrene) produced under identical conditions (□).

growing chain and the hemibenzopinacolate "counter-radical" (see Fig. 1). If it is true, possibility of parallel homopolymerization initiated by this radical should be eliminated. However, the formation of a crosslinked graft copolymer at relatively low conversions indicates that the association cited above

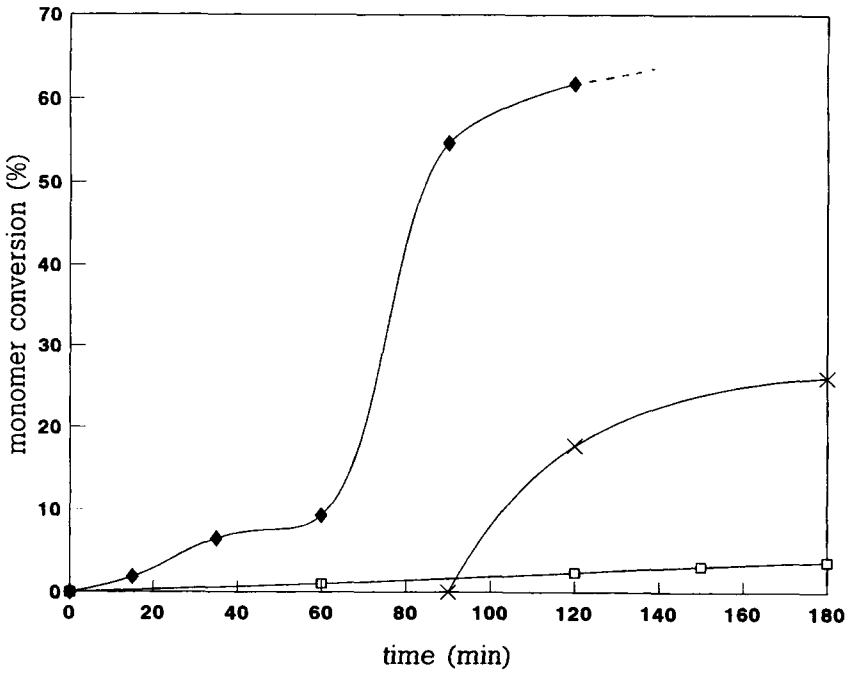

Figure 4 Conversion vs. time for the bulk polymerization of methylmethacrylate initiated with poly(styrene)-initiator 9i (♦), content of crosslinking copolymer (×), and thermal poly(methylmethacrylate) produced under identical conditions (□).

Table IV Composition of Products Obtained with the Poly(styrene)-initiator (9i) and Poly(methylmethacrylate)-initiator (10i) at 90°C and Different Polymerization Times

Time (Minutes)	Monomer Conversion (%)	Composition (%)			
		Macroinitiator	Homopolymer	Crosslinked Graft-Copolymer	Soluble Graft-Copolymer
PMMA (10i)					
60	14.53	18.88	3.53	77.58	0.51
150	23.37	22.85	5.44	71.71	0.00
210	23.96	20.44	7.26	70.96	1.34
240	25.71	18.77	8.30	69.27	3.66
PS (9i)					
15	1.87	66.15	18.86	—	20.70
60	9.27	37.74	22.53	—	45.54
90	54.76	0.19	—	4.07	26.33
120	61.81	0.78	13.24	53.68	32.30
180	54.19	0.54	35.67	45.08	18.75

is so weak that it allows bimolecular coupling between growing chains. This assumption is also supported by the formation of small amounts of homopolymers detected during graft polymerizations, which are probably produced by the free hemibenzopinacolate radical. Therefore, under experimental conditions used here, a suggested mechanism of living radical polymerization does not allow satisfactory explanation of the results obtained, and needs to be corrected in accordance with the new data. In this respect, recent experiments concerninig graft copolymerizations initiated with the polymeric initiators presented in this article, at temperatures in the order of 130°C, have demostrated that the living character of benzopinacolates groups depends strongly on temperature. Hence, graft copolymers PS-*g*-PMMA and PMMA-*g*-PS have been obtained without gel.

In spite of the network formation, the synthesis of graft copolymers via multifunctional polymeric initiators was possible with efficiences raising 80%. This method of synthesis have been used to prepare graft copolymers of styrene and methylmethacrylate, but other vinyl monomers can be polymerizated to prepare new copolymers by free radical graft polymerization. Future work will be devoted to the investigation of the dependence of the gel formation of graft copolymerizations on temperature in order to find conditions preventing this undesirable phenomenon.

Acknowledgement is made to the Consejo Nacional de Ciencia y Tecnología (CONACYT) for financial support (Contract No.1762-E9210).

REFERENCES

1. R. Calas, N. Duffaut, C. Biran, M. P. Bourgeois, F. Pisciotti, and M. J. Dunogues, *C.R. Acad. Sci., Paris,* **267,** 322 (1968).
2. D. Braun and R. Rengel, *Angew Makromol. Chem.,* **98,** 265–277 (1981).
3. H. Hillgartner, W. P. Neumann, and B. Schroeder, *Liebigs Ann. Chem.,* **144,** 586–599 (1975).
4. J. V. Crivello, J. L. Lee, and D. A. Conlon, *J. Polym. Sci., Polym. Chem. Ed.,* **24,** 1251–1279 (1986).
5. R. Guerrero-Santos, Ph. Chaumont, J. E. Herz, and G. Beinert, *Eur. Polym. J.,* **28,** 1263–1268 (1992).
6. T. Otsu, M. Yoshida, and T. Tazaki, *Makromol. Chem., Rapid Commun.,* **3,** 133–140 (1982).
7. R. Guerrero-Santos, Ph. Chaumont, J. E. Herz, and G. Beinert, *Eur. Polym. J.,* to appear.
8. M. Fineman and S. D. Ross, *J. Polym. Sci.,* **5,** 259–265 (1950).
9. F. R. Mayo and F. M. Lewis, *J. Am. Chem. Soc.,* **66,** 1594 (1944).
10. Von D. Braun, W. Newmann, and J. Faust, *Makromol. Chem.,* **85,** 143–154 (1965).

Received August 22, 1994
Accepted February 14, 1995