Redox Initiation of Copolymerization of Styrene with Hydroxyl Terminated Polybutadiene Using Ce(IV) as an Oxidant

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ABSTRACT: Radical polymerization of styrene (St) with hydroxyl-terminated polybutadiene (HTPB) using Ce(IV) as an oxidant was carried out under nitrogen atmosphere. The formation of styrene–butadiene block copolymer was confirmed by ^{1}H-NMR and IR spectroscopy. The variation in reaction parameters affected the yield of the product. St homopolymer formation under the reaction conditions used is ruled out. Crosslinking of polybutadiene chains through the styryl radical on growing block copolymer chains is suggested from viscosity and swelling measurements. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 244–256, 2002

Key words: polybutadiene; polystyrene; radical polymerization; copolymerization; block copolymers

INTRODUCTION

Homopolymers and block copolymers are readily produced from a variety of monomers by radical polymerization, which is characterized by its high rate and highly reactive nature of the chain carrier. Because the activity of the propagating radical in a homogeneous system cannot be preserved for the preparation of block or graft copolymers by a radical mechanism, one of the possible means of solving this difficulty is to generate a macroradical from a suitably substituted polymer in the presence of a second monomer. If a functionally terminated polymer is synthesized from one monomer and this preformed block is used as a redox system in conjunction with an oxidant for the polymerization of another vinyl monomer to form the block copolymer, such a system may be termed a macroredox initiator system. Recently, redox systems in block copolymer synthesis were reviewed.[1]

Ce(IV) salt–alcohol system is a classical redox initiator system.[2] Mino and Kaizerman[3] observed for the first time that oxidation of alcohols by Ce(IV) ion proceeds by a single electron transfer:

$$R_{cell}OH + Ce^{4+} \rightleftharpoons [Complex] \rightarrow$$
$$R_{cell}O^* + Ce^{3+} + H^+ \quad (1)$$
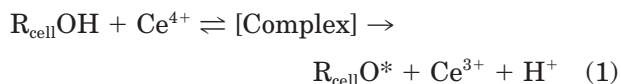
It is well known that Ce(IV) ion–alcohol redox systems are capable of initiating radical polymerization of vinyl monomers, as are the redox systems consisting of Ce(IV) ion and polymers with alcoholic hydroxyl groups, such as polyvinyl alcohol and cellulose.[3] Ce(IV) was found to be reactive

toward the hydroxyl groups of many polysaccharides to the graft copolymerization. Therefore, it is predictable that a block copolymer can be produced when Ce(IV) reacts with a prepolymer end-capped with hydroxyl groups in the presence of a vinyl monomer. Ce(IV) ion was used in conjunction with macromolecules which contained methylol groups at both chain ends, similar to poly(ethylene oxide),[4–7] poly(propylene oxide glycol),[8] poly(N-vinyl-2-pyrrolidone) with hydroxyl end groups,[9] poly(azoesters),[10,11] 4,4′-azobis(4-cyanopentanol),[12] poly(ethylene glycol),[13] and ketonic resin[14] to obtain block copolymers. Through lowering the reaction temperature and controlling the reaction time, the amount of homopolymer formation was reduced.[8]

Most of the studies with Ce(IV) ion-initiated block or graft copolymerization were carried out in aqueous solutions with water-soluble monomers. Almost no report is available either on homopolymerization or graft copolymerization of styrene (St) with Ce(IV) initiation, although some graft copolymerizations were observed with mixtures of active monomers such as MMA or AN.[15] St could not be homopolymerized through Ce(IV)/thiourea-initiated aqueous polymerization system.[16] Similarly, polystyrene could not be grafted onto carbon black by radical graft polymerization initiated by Ce(IV) and carbon black having alcoholic hydroxyl groups redox system.[17]

The present article reports the block copolymerization of St with butadiene through hydroxyl-terminated polybutadiene (HTPB)–Ce(IV) redox-initiator system.

EXPERIMENTAL

Materials

HTPB ($M_n \sim 2000$), a gift from Vikram Sarabhai Space Center, Thiruvananthapuram, Kerala, India, was purified by washing repeatedly with methanol, after which it was vacuum dried. The monomer, St (John Baker Inc., CO), was vacuum distilled prior to use. Ceric sulfate (CDH, Bombay, Maharastra, India) of analytical reagent (AR) grade was used as received. Sulfuric acid, methanol, petroleum ether (60–80°C), and other solvents (all from Qualigens, Bombay, Maharastra, India) were used without further purification.

Synthesis of Block Copolymers

The reaction vessel was a Pyrex glass test tube with a length of 12 cm and an inner diameter of 2.5 cm with a ground glass joint, fitted with a cone with inlet and outlet tubes. HTPB and St were taken in this reaction vessel and kept in a serological bath (with a temperature control ± 0.5°C) maintained at the required temperature and oxygen-free dry nitrogen gas was bubbled into it. Ceric sulfate solution was prepared freshly each time in sulfuric acid diluted with methanol, deaerated, and thermostated separately. It was then added to the reaction vessel quickly in about 5 s. Nitrogen gas was continuously bubbled through the reaction mixture. Finally, after a certain time period, the reaction was arrested by adding a known excess amount of ferrous ammonium sulfate solution so that all the excess ceric ions were reduced to the cerous ions. The product obtained was washed thoroughly with dilute sodium hydroxide solution, then with water, and finally with petroleum ether to remove the unreacted HTPB, St, sulfuric acid, and the other inorganic materials added to the reaction mixture. The product was dried initially in vacuum and then in air and weighed to a constant weight. The extent of the reaction of St was determined gravimetrically in terms of percentage yield, evaluated by using the relationship:

Yield of the product (%)

$$= \frac{\text{weight of the product}}{\text{weight of HTPB} + \text{weight of styrene}} \times 100$$

(2)

To examine the effect of various parameters (such as time, temperature, and concentration of various components of reaction mixture), several experiments were performed varying the examined parameter and keeping the other ones constant.

Preparation of Sample Used in the Determination of Extent of Crosslinking

The reactants were scaled up by 10 times for the typical set. Twenty grams (0.37 mol) HTPB, 13 g (0.125 mol) St, 2.0 g (6.02 mmol) ceric sulfate, 100 mL H_2SO_4, and 100 mL methanol were used and the reaction was arrested, after 1 h, by the addition of excess of ferrous ammonium sulfate and the crude product thus obtained was washed thoroughly with water and aqueous NaOH repeatedly and finally with water to remove the inorganic materials. The resulting product was extracted subsequently with petroleum ether and benzene for 48 h with each solvent. The solutions and
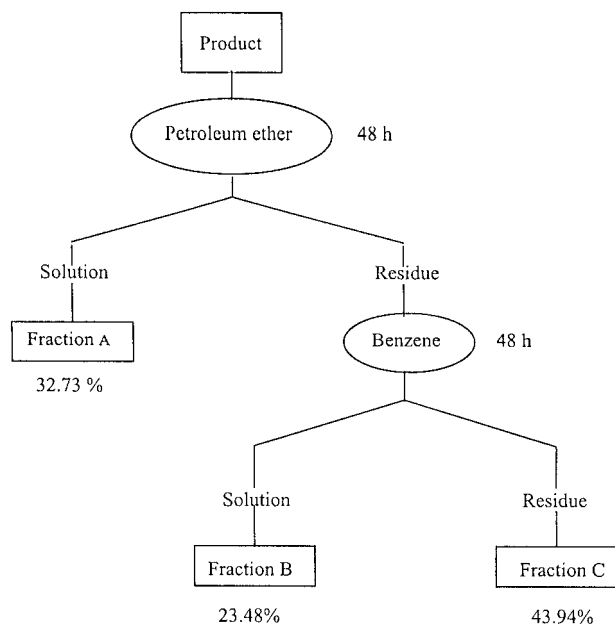
Scheme 1 Selective extraction scheme.

residues were separated. The solvents were removed by vacuum evaporation and the fractions weighed until constant weight.

The fractionation experiment, carried out to determine the proportion of the crosslinked product, is presented schematically in Scheme 1. The percentages mentioned relate to the initial amount of the product used.

Measurements

Infrared spectra of some selected samples of block copolymers, HTPB, and an authentic sample of polystyrene were recorded on a Perkin–Elmer model 1430 spectrophotometer (Perkin–Elmer Cetus Instruments, Norwalk, CT) by using KBr as dispersant. ^{1}H-NMR spectrum of a representative sample (run 1, Table I) was recorded on a Bruker DRX-300 FT-NMR spectrometer (Bruker Instruments, Billerica, MA) in $CDCl_3$ solution using TMS as an internal standard.

Viscometry studies were performed at 27°C by using an Ubbelohde viscometer in chloroform solution. The Huggins' and the Kraemer's equations [eqs.(3) and (4)] were used to determine intrinsic viscosity $[\eta]$, Huggins' constant k', and Kraemer's constant k''

$$\eta_{sp}/C = [\eta] + k'[\eta]^2\, C \tag{3}$$

$$\ln \eta_r/C = [\eta] + k''[\eta]^2\, C \tag{4}$$

where η_{sp} and η_r are specific and relative viscosities, respectively, and C is the concentration of polymer in grams per 100 mL. The results of both equations were plotted using the same graph. The point of intersection of both lines at the ordinate was taken as the intrinsic viscosity.

Swelling Measurements

Samples of the crosslinked product measuring 0.1 g, the fraction C (Scheme 1), insoluble in benzene, were immersed in 50 mL of various solvents for 48 h to attain equilibrium swelling. The samples were then taken out from the solvent bath, pressed between filter paper to remove the excess of solvent, and weighed immediately. The swelling coefficient of the crosslinked product (Q) was calculated by[18]

$$Q = \frac{m - mo}{mo} \times \frac{1}{d} \tag{5}$$

where m is the weight of swollen polymer, mo is the weight of polymer taken initially, and d is the density of the solvent used. The characteristic parameters for the solvents were obtained from literature.[19a]
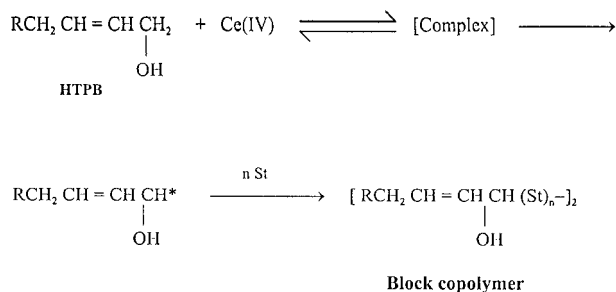
RESULTS AND DISCUSSION

The polymerization of St was carried out by a redox system consisting of Ce(IV) and hydroxyl-

Table I   Effect of Time and Temperature on Yield of Product[a]

Run No.	Time (min)	Temperature (°C)	Yield (%)
1	05	35	[b]
2	15	35	47.3
3	30	35	72.4
4	60	35	85.5
5	90	35	83.6
6	120	35	85.5
7	150	35	85.5
8	180	35	85.2
9	60	30	[b]
10	60	40	90.0
11	60	45	93.0
12	60	50	94.9

[a] HTPB, 37.04 mmol butadiene; styrene, 12.50 mmol; ceric sulphate, 0.602 mmol; sulphuric acid, 10 mL; methanol, 10 mL.
[b] The product obtained was highly viscous rubbery liquid, fractionated with toluene; 98% was soluble in toluene and 2% was insoluble.

RCH₂ CH = CH CH₂   +   Ce(IV) ⇌ [Complex] ⟶

(Scheme structures with OH, HTPB)

RCH₂ CH = CH CH*   —(n St)→   [RCH₂ CH = CH CH (St)ₙ—]₂

Block copolymer

Scheme 2 Formation of block copolymers of [—B—S—]ₓ type, where B and S represent polybutadiene and polystyrene blocks, respectively. (For the sake of convenience of presentation, only one of the terminal butadiene units of HTPB is shown.)

terminated polybutadiene (HTPB) ($M_n \sim 2000$) in methanolic sulfuric acid medium. The polymerization is expected to proceed according to Scheme 2.

The details of the reaction conditions and the yield of product obtained are summarized in Tables I and II. It was observed that the reaction time affected the yield. However, the reaction was sufficiently fast; there was no induction period as evidenced by the appearance of haziness in the clear reaction mixture immediately after addition of ceric sulfate solution and 1 h polymerization sufficed as indicated by the curve in Figure 1.

Effect of Temperature

The polymerization was studied in the 30–50°C range (Fig. 2). Some experiments were performed to investigate the possibility of the formation of St homopolymer and/or crosslinked polybutadiene under the reaction conditions employed. It was noticed that in the absence of St, HTPB crosslinked to yield a brittle product insoluble in petroleum ether at 50°C. However, at 35°C in 1 h, an emulsion was obtained, most of which dissolved gradually on stirring with petroleum ether and about 12% of HTPB remained as an insoluble brittle residue. The results are presented in Table III. Further, at 50°C, in the absence of HTPB, some St homopolymer was formed in 30 min, whereas the latter was not obtained at 35°C even in 1 h. Hence, the other experiments were carried out at 35°C to eliminate the possibility of homopolystyrene formation and to minimize crosslinking of HTPB.

Effect of Concentration of Ceric Sulfate

The effect of concentration of ceric sulfate on the yield of product was studied (run 4 in Table I and

**Table II   Effect of Concentration of Ceric Sulphate, Sulphuric Acid, Methanol, and Styrene on Yield of Product[a]**

Run No.	Styrene (mmol)	Ceric Sulphate (mmol)	H_2SO_4 (mL)	Methanol (mL)	Yield (%)
13	12.5	0.750	10.0	10.0	87.6
14	12.5	0.500	10.0	10.0	83.1
15	12.5	0.375	10.0	10.0	82.6
16	12.5	0.250	10.0	10.0	[b]
17	12.5	0.125	10.0	10.0	[b]
18	12.5	0.602	15.0	10.0	89.7
19	12.5	0.602	12.5	10.0	88.2
20	12.5	0.602	7.5	10.0	68.8
21	12.5	0.602	5.0	10.0	[b]
22	12.5	0.602	10.0	15.0	[b]
23	12.5	0.602	10.0	7.5	89.7
24	12.5	0.602	10.0	5.0	[c]
25	38.5	0.602	10.0	10.0	[d]
26	28.8	0.602	10.0	10.0	[d]
27	19.2	0.602	10.0	10.0	38.3
28	7.2	0.602	10.0	10.0	70.6

[a] HTPB, 37.04 mmol of butadiene; temperature, 35°C; reaction time, 60 min.
[b] The copolymer obtained was highly viscous rubbery liquid, completely soluble in petroleum ether.
[c] Ceric sulphate was not completely soluble. The reaction mixture charred after 5 min.
[d] The reaction mixture charred after 15 min.
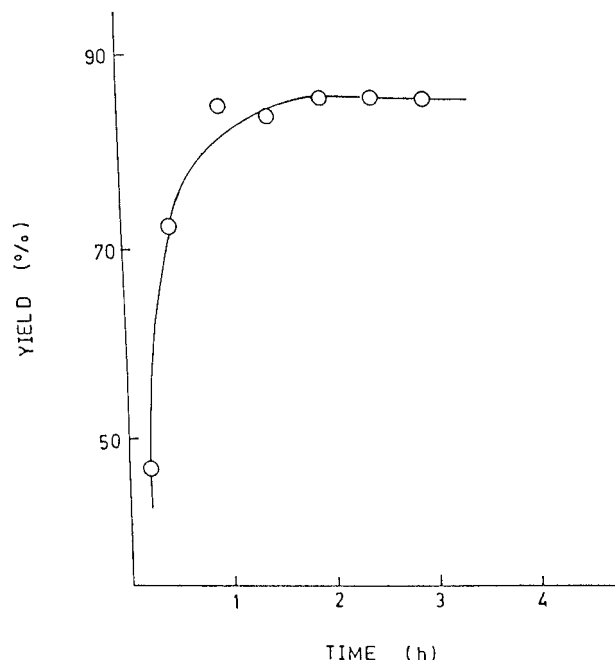
Figure 1 Effect of reaction time on percentage yield (HTPB, 37.04 mmol; styrene, 12.50 mmol; ceric sulfate, 0.602 mmol; H_2SO_4, 10 mL; methanol, 10 mL; temperature, 35°C).

runs 13 to17 in Table II). The results are graphically presented in Figure 3. It is evident that the yield increased with the increase in concentration of ceric sulfate, which is quite logical. However, conclusive results could not be obtained on further increase in ceric sulfate concentration as its solubility is limited in methanolic sulfuric acid. An amount of ceric sulfate higher than 0.75 mmol was not completely soluble in the required quantity of methanolic sulfuric acid.

Effect of Monomer Concentration

The monomer concentration had a prominent influence on the yield of the product (runs 4 and 25 to 28 in Tables I and II, respectively). When the amount of St was increased, there was a sharp increase in the yield but upon reaching an optimum level it dropped steeply (Fig. 4). The use of still higher concentrations resulted in charring of reaction mixture after 15 min.

A curve similar to that in Figure 4 was obtained by Abere et al.[20] in their study of heterogeneous solution polymerization of St dissolved in methanol, for dependence of rate of polymerization on monomer concentration in the initial concentration range. They explained that the en-

hanced rate at lower concentrations of monomer is due to the reduction in the rate of bimolecular termination caused by heterogeneity of the medium.

HTPB is insoluble in methanol; however, it is soluble in St. At lower concentrations of St, the system is heterogeneous and the chances of collision between terminal methylol groups of HTPB and the oxidant Ce(IV) present in different phases are rare. Increments in the amount of St gradually homogenize the reaction mixture and the yield of copolymer increases. However, after reaching a maximum, it decreases again. This may be attributed to the effect of increasing dilution on the propagation step or to the increase in rate of bimolecular termination. Radical polymerization of St in solution has been extensively studied. Several interesting results were published on the effect of reaction medium. In the polymerization of St, the propagation rate constant was shown to decrease experimentally with the increasing dilution.[21] This observation is in good agreement with the hot radical theory.[22,23] The theory of hot radical was based on the fact that the propagating radical contains, in the moment of its formation, the reaction heat and activation energy of exothermal elementary process of chain propagation in the form of vibrational energy. The vibrationally excited hot radical formed in the propagation step can be deactivated in collisions with the components of the reaction mixture (monomer and solvent).
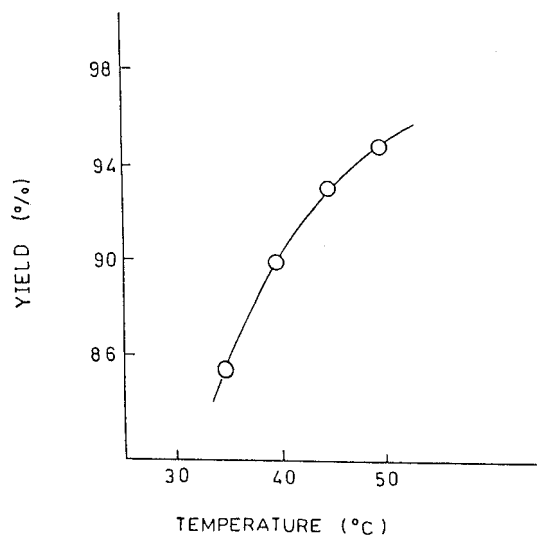
Figure 2 Effect of temperature on percentage yield (HTPB, 37.04 mmol; styrene, 12.50 mmol; ceric sulfate, 0.602 mmol; H_2SO_4, 10 mL; methanol, 10 mL; time, 1 h).

Table III   Results of Polymerization in Absence of Any One Component[a]

HTPB[b] (mmol)	Styrene (mmol)	Temperature (°C)	Time (min)	Product
37.04	—	50	30	Brittle product
—	12.5	50	30	Polystyrene ($\sim$ 1%)
37.04	—	35	30	Emulsion dissolved on stirring in petroleum ether
—	12.5	35	30	No solid product
7.04	—	35	60	Brittle product (12%)
—	12.5	35	60	No solid product

[a] Ceric sulphate, 0.602 mmol; sulphuric acid, 10 mL; methanol, 10 mL.
[b] mmol of butadiene units.

The charring of the reaction mixture at higher concentrations of St may be due to autoacceleration. It is widely accepted in literature that in St polymerization the chain termination takes place exclusively by the recombination of polymer radicals.[23,24] Bamford et al.[25] concluded that in all the cases of heterogeneous polymerization the reactions are characterized by low rates of termination and hence by high rates of reaction together with high degrees of polymerization. The barrier to termination may be solid polymer or an interface. Ham[24] stated that when the monomer concentration was increased to a higher value, a great acceleration of rate of polymerization was encountered. The autoacceleration has significant implications for the polymerization of monomers that yield insoluble polymers. The rapid increase in polymerization rate often leads to a substantial increase in the temperature of the polymerization because the dissipation of the heat of polymerization becomes quite inefficient with the viscosity increase. The effect cannot be eliminated, however, by keeping the temperature uniform throughout the reaction. It is also suggested that the increased temperature may favor the formation of homopolymer, as it was observed that higher temperatures promoted the formation of homopolystyrene.

Effect of Methanol

Methanol was used as a diluent for sulfuric acid and St. At lower concentrations of methanol, ceric sulfate was not completely soluble, autoacceleration effect was pronounced, and the reaction mixture was charred. In the limiting range (7.5–10
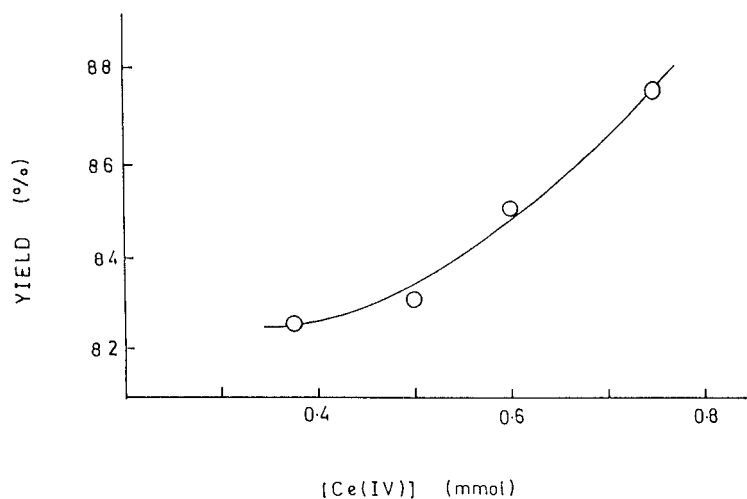
Figure 3 Effect of concentration of ceric sulfate on percentage yield (HTPB, 37.04 mmol; styrene, 12.50 mmol; H₂SO₄, 10 mL; methanol, 10 mL; temperature, 35°C; time, 1 h).
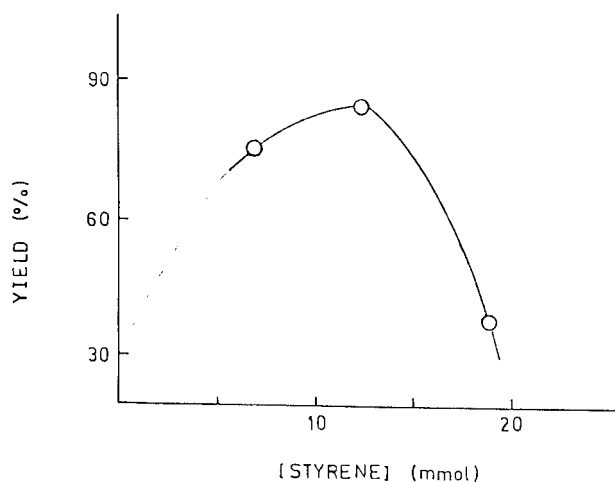
Figure 4 Effect of concentration of styrene on percentage yield (HTPB, 37.04 mmol; ceric sulfate, 0.602 mmol; H_2SO_4, 10 mL; methanol, 10 mL; temperature, 35°C; time, 1 h).

mL), the product insoluble in petroleum ether could be obtained. However, further increase in volume of methanol yielded a product soluble in petroleum ether. Although methanol was used here as the diluent for St to control the autoacceleration, the growth of macromolecular chains is limited by the precipitation power of methanol.

Bross et al.[26] studied the macroradical cage phenomena in the case of hydroalcoholic solutions of poly(methyl methacrylate). Their results demonstrated the existence of phenomenon of encagement of the macroradicals that are to be found more or less imbricated in a viscous environment favorable to propagation reactions and unfavorable to termination reactions. Beyond a given concentration range, the favorable environment no longer exists.

Along the same lines, it is suggested that in the optimum concentration range of methanol, macroradical cage phenomena may be predominant, which favors the propagation reactions leading to growth of St units on HTPB. However, increase in volume of methanol results in a less viscous medium, the termination reactions predominate, and a lesser number of St units are associated in the block copolymer; hence, it is completely soluble in petroleum ether. It may be suspected that the reaction of methanol with Ce(IV) to produce radicals may occur more readily than reaction with HTPB considering the molecular size, but to the best of our knowledge, there is no report in literature for Ce(IV)–methanol initiator system. Further, on excluding HTPB only from the reac-

tion mixture, St homopolymer could not be obtained. If a radical could be generated on methanol through chain transfer or if the initiating ability of the Ce(IV)–methanol pair was significant, the total yield (which includes St homopolymer also) would have increased with the increasing amount of methanol. The actual observation contradicts this possibility because with the use of a large volume of methanol the product obtained was a highly viscous rubbery emulsion which was soluble in petroleum ether. St homopolymer is not soluble in petroleum ether. HTPB does not form emulsion with petroleum ether; it is soluble in the latter.

Effect of Sulfuric Acid

Figure 5 is indicative of an increase in yield of product with increasing concentration of sulfuric acid. However, if the amount of sulfuric acid is further increased, charring of the reaction mixture is observed as a consequence of the greatly enhanced rate, resulting in autoacceleration. It has been shown by different investigators that various reactive species such as Ce^{4+}, $CeSO_4^{2+}$, $Ce(SO_4)_2$, $Ce(SO_4)_3^{2-}$, $Ce(HSO_4)_3^+$, and $H_2Ce(SO_4)_4^{2-}$ exist in aqueous sulfuric acid medium.[27,28] With increasing sulfuric acid concentration, more sulfated complex will predominate. Pramanick et al.[27] concluded for ceric salt/thiourea redox initiation system for vinyl polymerization that electron transfer from thiourea to ceric species will be facilitated progressively as it changes from neutral $Ce(SO_4)_2$ to the negatively charged $Ce(SO_4)_3^{2-}$ species with increasing sulfuric acid concentration; consequently, the rate of polymerization is enhanced. The observation in the present study can also be explained similarly.

Characterization

The IR spectra of fraction A and B (Scheme 1) extracted by petroleum ether and benzene, respectively, are depicted in Figure 6. The strong and broad absorption bands due to ν_{OH} at 3446 cm^{-1} in fraction A and at 3413 cm^{-1} in fraction B are indicative of the presence of hydroxyl groups of HTPB. The strong absorption due to out-of-plane C—H bending of HTPB appears at 968 cm^{-1} in both cases. The appearance of alkane CH stretching at 2920–2846 cm^{-1} and alkene C=C vibrations at 1637 cm^{-1} are further suggestive of the presence of polybutadiene component in block copolymer. The two characteristic peaks of monosubstituted benzene ring of the polystyrene com-
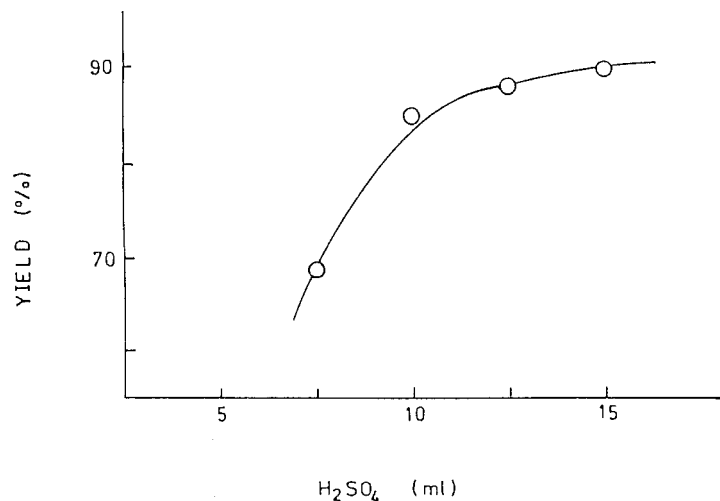
Figure 5 Effect of volume of sulfuric acid on percentage yield (HTPB, 37.04 mmol; styrene, 12.50 mmol; ceric sulfate, 0.602 mmol; methanol, 10 mL; temperature, 35°C; time, 1 h).

ponent in the block copolymer appears at 752,696 and 767,698 cm^{-1} in fractions A and B, respectively. Further, the presence of aromatic C—H stretching at 3060–3016 cm^{-1} skeletal vibrations involving $\nu_{C—C}$ within the ring at 1616 cm^{-1}, and a doublet in the 1500–1400 cm^{-1} region and the characteristic absorption pattern owing to the monosubstituted benzene ring at 2000–1650

cm^{-1} region, are indicative of the polystyrene component in the block copolymer.

Thus, it is apparent that in the fraction extracted by petroleum ether as well as benzene, both the components, the polybutadiene blocks and the polystyrene blocks, are present; however, the contribution is different. Fraction A has a greater contribution from HTPB, as evident from
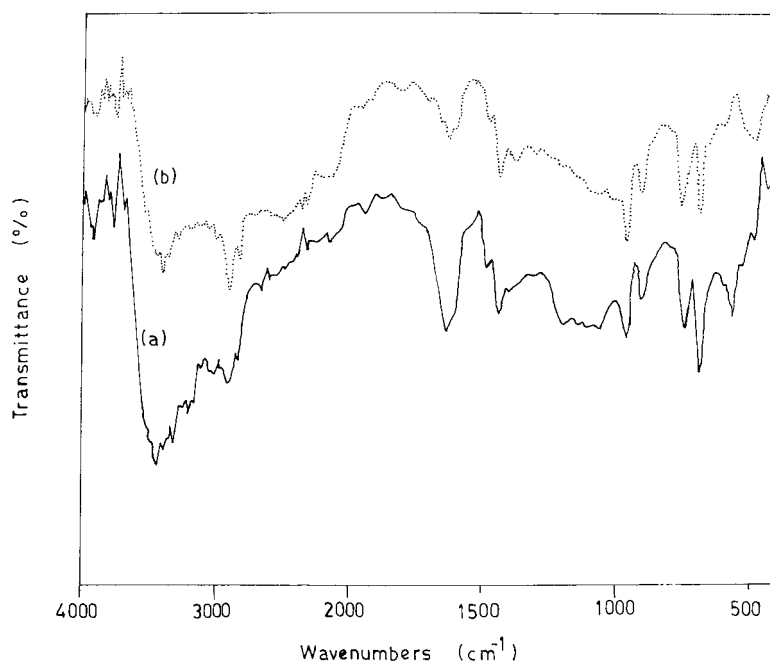
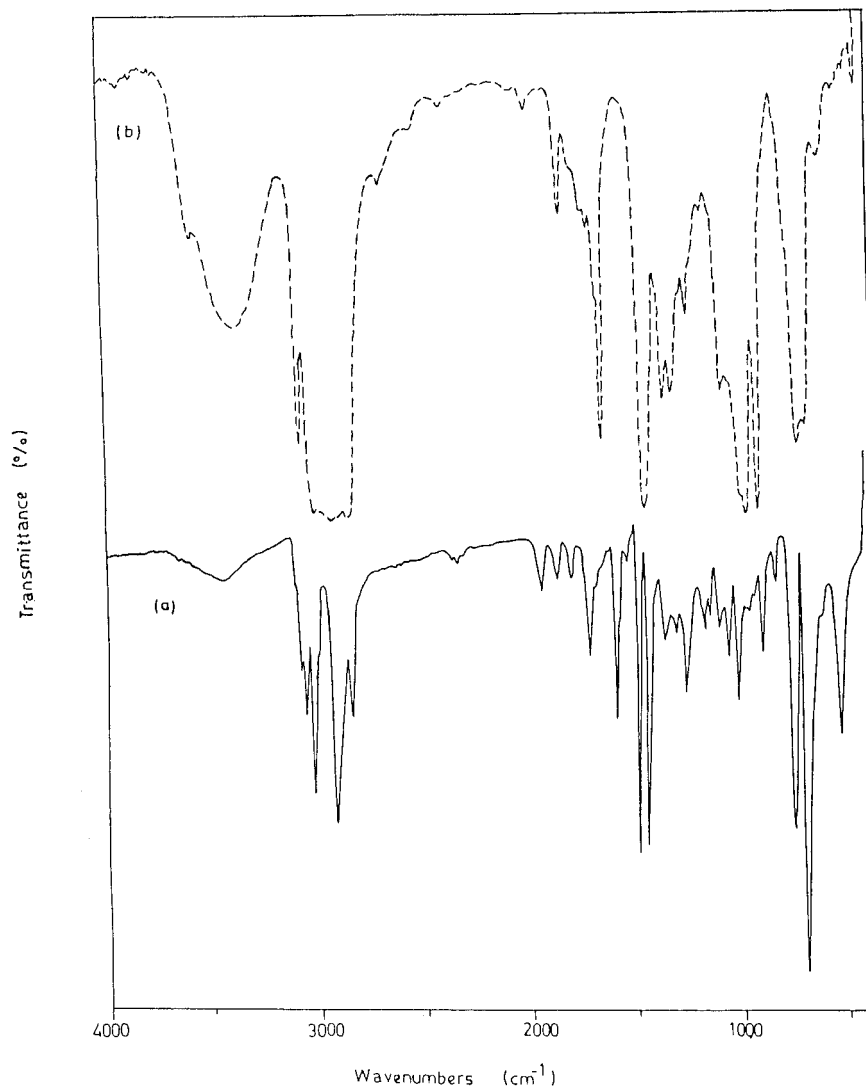**Figure 6** IR spectra of (a) fraction A (Scheme 1); (b) fraction B (Scheme 1).

Figure 7 IR spectra of (a) polystyrene; (b) HTPB.

the more intense peak due to the hydroxyl group. An approximately quantitative contribution from each component can be determined by comparison of the intensities of the bands characteristic of either component. The ν_{C-H} of the —CH=CH— group of HTPB (1637 cm^{-1}) and out-of-plane C—H deformation characteristic of monosubstituted aromatic ring (767 cm^{-1}) were selected for this comparison and the proportion was calculated by using the literature method.[29] The proportions of butadiene and St for fractions A and B were calculated to be 1.409 : 1 (58.5 : 41.5) and 1 : 2.133 (32 : 68), respectively. One may argue that the IR spectrum is by no means evidence of block copolymerization. Physical blends of same composition as block copolymer will give the

same IR spectra. However, it was found that under the present experimental conditions, formation of homopolystyrene is almost negligible. Further, the two constitutive components could not be separated by the use of selective solvents.

Estenoz et al.[30] thoroughly studied the bulk polymerization of St in the presence of polybutadiene and proposed an extended kinetic mechanism for monomer thermal initiation, chain transfer to the monomer, and the gel effect. They commented that with the present analytical technology it is impossible to verify the predicted distribution for each of the generated copolymer topologies. Even the analysis of total copolymer is complicated because of the impossibility of quan-
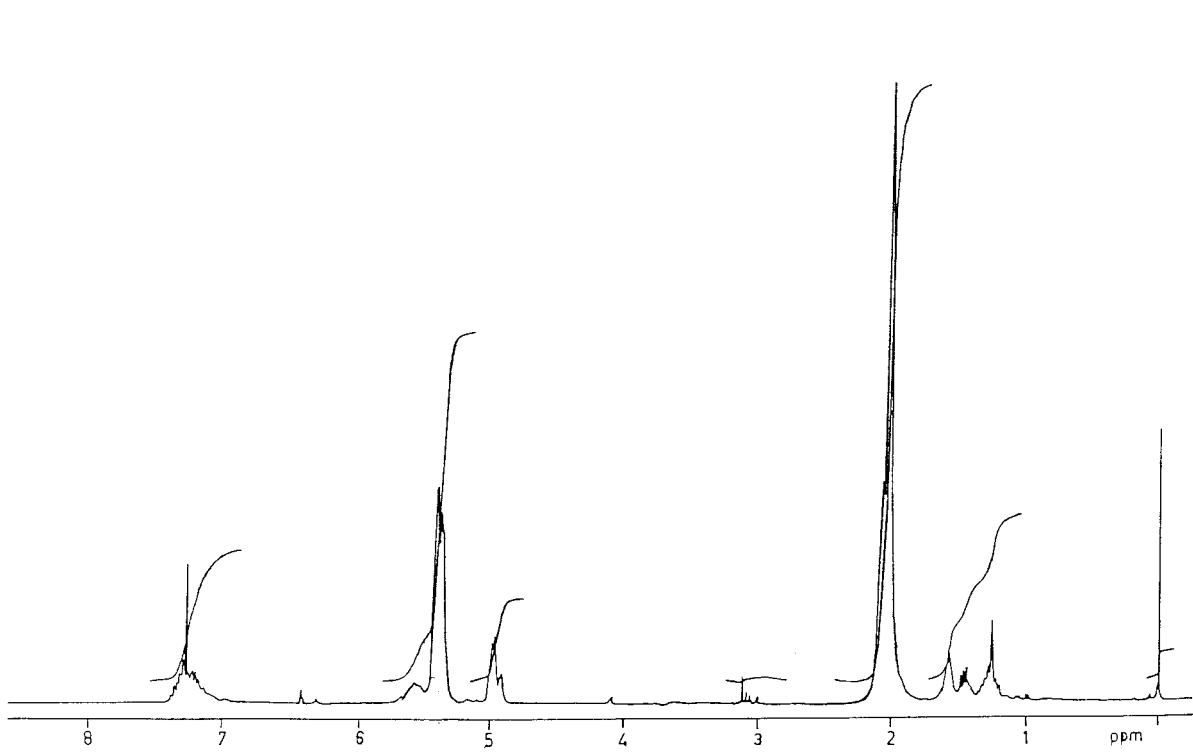
Figure 8 ^{1}H-NMR spectrum of block copolymer.

titatively extracting the occluded PS and PB homopolymer from the copolymer.

HTPB and a sample of polystyrene (IR spectra depicted in Fig. 7), prepared by bulk photopolymerization of St, were dissolved separately in benzene and the solutions were mixed. The solution was then magnetically stirred for 5 h and kept overnight. Then, the solvent was vacuum evaporated. In the resulting material, HTPB remained in the usual fluid form and polystyrene separated as tiny granules which could be mechanically separated. However, the products obtained by macroredox polymerization technique did not exhibit any such macroscopic segregation; hence, the block copolymer formation is inferred from the physical appearance also.

The best characterization information was obtained from ^{1}H-NMR in CDCl$_3$ solution (Fig. 8) for the fraction soluble in toluene of a representative sample. A summary of the NMR data is given in Table IV. On comparison of intensities of aromatic protons on St units and methylene protons on butadiene units, the butadiene-to-styrene ratio in block copolymer was calculated to be 5.77 : 1 ($\sim$ 85 : 15%). NMR data has been used for the calculation of copolymer composition by other researchers also.[31,32] This sample was prepared

in a shorter reaction time (5 min), whereas the fraction A and B were obtained after 1 h of reaction. Hence, the different proportions calculated from IR and NMR data are definite proof that with the increase in reaction time the proportion of St in the block copolymer increased.

The viscosity measurements were carried out in chloroform solutions for the fraction soluble in petroleum ether and benzene (fractions A and B, respectively, in Scheme 1) and also for HTPB for comparison. The results are depicted in Table V and Figure 9. The values obtained for Huggins' constant, k', and Kraemer's constant k'' are well in agreement with the acceptable value in good solvent and the constants satisfy the condition of eq. (6) also:

Table IV   NMR Spectral Data of Butadiene–Styrene Copolymer at 300 MHz

Proton	Frequency (ppm)	Relative Intensity
Aromatics	7.28–7.26	1.00
Vinyls	5.41–5.38	2.23
Methylene (Butadiene units)	2.07–2.03	4.62

Table V   Intrinsic Viscosity, Huggins' and Kramer's Constants for the Fractionated Samples of Block Copolymer in Chloroform at 27°C

Sample No.	Sample	$[\eta]$	k'	k''
1	Fraction A[a]	0.250	0.3200	0.1862
2	Fraction B	0.182	0.3623	0.1449
3	HTPB	0.138	0.3571	0.1505

[a] Fractions obtained from the selective extraction of the product obtained in determination of crosslinking (Scheme 1).

$$k' + k'' = 0.5 \qquad (6)$$

It is known that for flexible polymers in good solvents, k' is often near 0.35.[33] The k' values for the petroleum ether fraction and the benzene fraction are indicative of the flexible nature of these polymers. A slightly higher value for the fraction B perhaps suggests its branched structure or lightly crosslinked nature. Further, it was expected that the benzene fraction must have higher molecular weight, hence, should exhibit a higher value for $[\eta]$, whereas the actual observation is in contradiction. Probably this is due to the different molecular architecture. A branched system behaves differently from its linear counterpart.[34] The chain branching decreases the intrin-

Figure 9   Plot of η_{sp}/C or $\ln \eta_r/C$ versus C in chloroform at 27°C. The upper lines are for η_{sp}/C and the lower lines are for $\ln \eta_r/C$. (a) HTPB; (b) fraction B (Scheme 1); (c) fraction A (Scheme 1).

sic viscosity.[35] It is possible that besides the linear bimolecular termination of growing polymer chains which leads to the formation of —[—S—B—]$_x$— type of linear block copolymer, the radical end of growing polymer may attack another chain to form the branched block copolymer.

The fraction which is insoluble in benzene (fraction C) is expected to be comparatively more heavily crosslinked. However, even this product shows a rubbery behavior. The rubbery behavior is attainable if the glassy domains act as crosslinks.[19b] Hence, it is suggested that the long chains of polybutadiene are interconnected by widely separated crosslinks formed by the glassy domains of polystyrene. This inference is further substantiated by the results from swelling measurements.

Equilibrium swelling of the fraction insoluble in benzene was determined in various solvents and the results are presented in Table VI and Figures 10 and 11. The solubility parameters δ, the square root of the cohesive energy density (CED), can be measured by the indirect method. It is expected that the maximum swelling will take place when δ of the polymer (δp) matches δ of the solvent (δs). Although equilibrium swelling may not be the best absolute measure of χ, the polymer–solvent interaction parameter, it is a very practical method and relates directly to an important application, namely, the selection of materials for use in the presence of solvents, and may also give an indirect idea about the possible geometry of the polymer.

A plot of the swelling coefficient Q, against δs values for various solvents (Fig. 10), exhibits a maxima ($\sim$ 8.95) corresponding to δp. It was shown[36] that

$$Q = Q_{\max} e - (\delta s - \delta p)^2 \phi s \qquad (7)$$

Thus, on plotting $[(1/\phi s)\ln(Q_{\max}/Q)]^{1/2}$ versus δs, a straight line is obtained which intersects the ab-
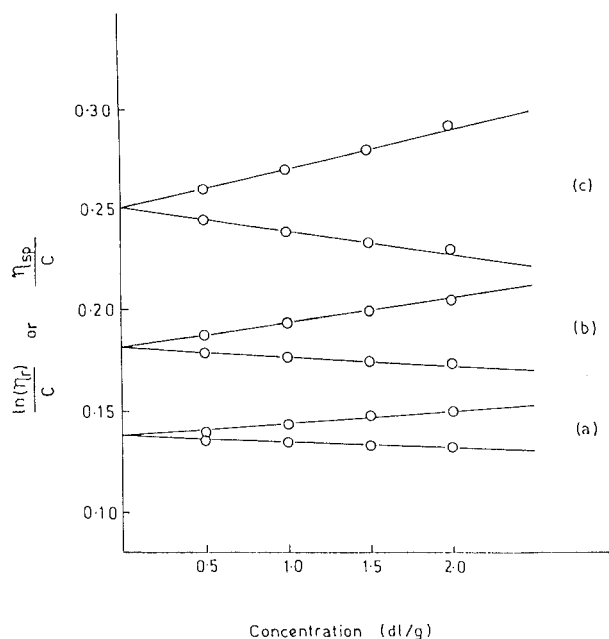
Table VI Swelling Behavior of the Fraction C (Scheme 1) in Various Solvents

Sample No.	Solvent	δs	Hydrogen Bonding Index	Q
1	n-Hexane	7.3	2.2	0.7634
2	Carbon tetrachloride	8.6	2.2	3.5132
3	Toluene	8.9	3.8	6.1485
4	Ethyl acetate	9.1	5.2	0.6659
5	Benzene	9.2	2.2	3.9818
6	Chloroform	9.3	2.2	8.7131
7	Methyl ethyl ketone	9.3	5.0	0.7500
8	Acetone	10.0	5.7	0.2525
9	N,N'-dimethyl acetamide	10.8	6.6	0.0854

scissa at a value corresponding to δp [i.e., 8.95 (Fig. 11)]. The values of δp obtained from both graphs (Figs. 10 and 11) are nearly the same.

The values of δp reported for polystyrene, polybutadiene, and butadiene–styrene (71.5 : 28.5) rubber are 9.1, 8.6, and 8.1, respectively.[37,38]

Thus, the value for δp for the crosslinked material is nearer to that for polystyrene rather than that for polybutadiene or random copolymer of styrene–butadiene. This suggests that crosslinked product is composed of —[—S—B—]$_x$— type of chains with a significant contribution from polystyrene blocks and such chains are interconnected at long intervals, accounting for the flexibility of the material.
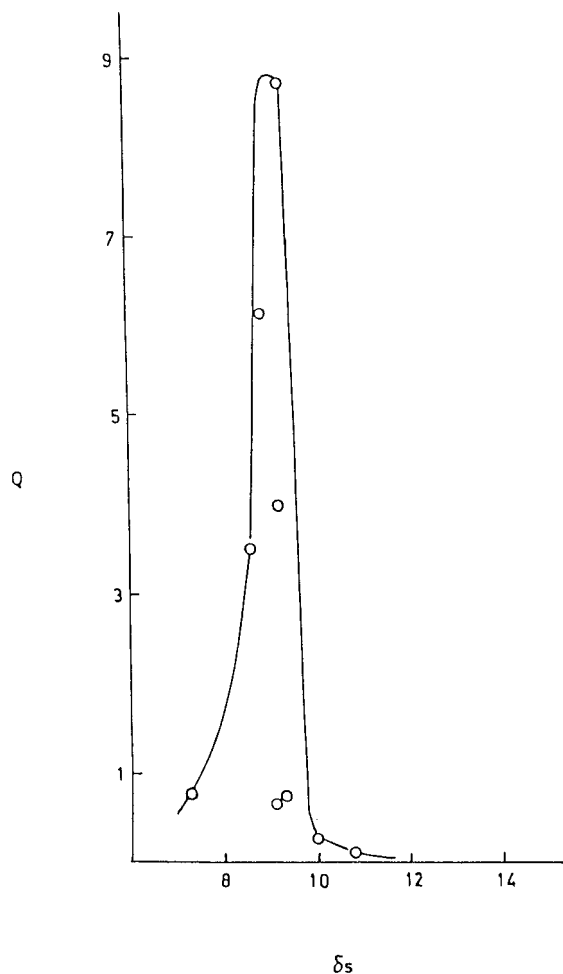
Figure 10 Plot of swelling coefficient Q versus δs.
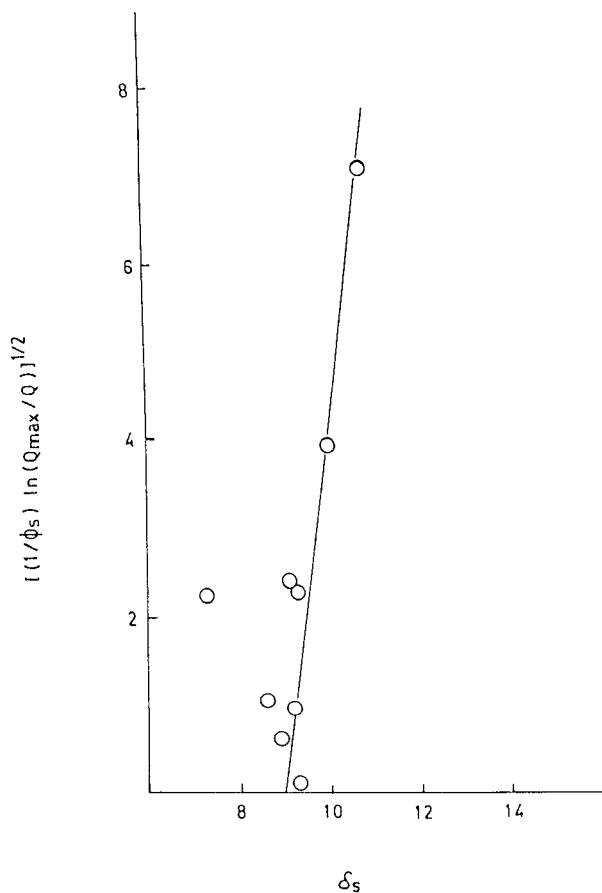
Figure 11 $[(1/\phi s)\ln(Q_{max}/Q)]^{1/2}$ versus δs plot.

CONCLUSION

HTPB–Ce(IV) forms an effective redox system for polymerization of St on polybutadiene block. By control of the reaction conditions (i.e., concentration of reactants, solvents, etc.) and time of reaction, a desired proportion of St can be introduced and an elastomeric fluid or an elastic solid could be obtained. The method can be very useful for the production of styrene–butadiene block copolymers for those applications where strictly monodisperse and linear elastomers are not desirable.

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