



# Synthesis and cross-linking of polyisoprene latexes

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## Abstract

Seeded and ab initio emulsion polymerizations of isoprene using redox initiation systems were investigated and suitable reaction conditions determined to prepare polyisoprene latexes with minimal cross-linking. Polymerizations initiated with the potassium persulfate/sodium bisulfite (KPS/SBS) redox couple had a significant inhibition period and low yield. Polymerizations initiated with the *tert*-butyl hydroperoxide/tetraethylene-pentamine redox couple showed reasonable yields and no apparent inhibition. It is postulated that the lipophilic nature of the *t*-butyl group plays a favorable role in the entry of hydroperoxide-initiated oligomeric radicals, while persulfate-initiated radicals are more likely to undergo aqueous phase termination before entry. The cross-linking reaction by benzoyl peroxide (BPO) at 70 °C was investigated using this lightly cross-linked polyisoprene latex. <sup>1</sup>H NMR and gel permeation chromatography results were consistent with a reaction mechanism in which the radicals formed by the decomposition of BPO react exclusively with polyisoprene to abstract a hydrogen atom, and the resulting radicals react by termination to form cross-links. No loss of double bonds was found, suggesting that radical formation is overwhelmingly achieved by hydrogen abstraction and cross-linking occurs by termination between two radicals. Cross-linking was accompanied by chain scission, which was observed only at the beginning of the reaction. At low weight-fractions of polymer, the rate of cross-linking was dependent on the concentrations of BPO and abstractable hydrogens in a manner consistent with the postulated mechanism.

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## 1. Introduction

In free-radical polymerization, the formation of covalent bonds between individual polymer chains to form a cross-linked network is caused primarily by hydrogen abstraction to create radicals on the backbones of pre-existing polymer chains, or addition to pendant vinyl groups where bifunctional monomers are present [1–4]. It is most important for polymers with readily abstractable protons [2,5–7]. The monomer isoprene shares with other dienes such as butadiene and chlorobutadiene a high likelihood of significant cross-linking, the occurrence of multiple modes of propagation, and the necessity of adding mercaptans to achieve a significant polymerization rate in emulsion polymerization (e.g. Refs. [8,9]). Polymers of these dienes may undergo either addition or abstraction with a radical arising from an initiator and the abstraction pathway is facilitated through the stability of the resulting allylic

radical [4]. The stability of the allylic radical can lead to a dramatic retardation in polymerization rate as these are terminated by short radicals rather than re-initiating polymerization, the phenomenon of ‘retardative chain transfer’ [10–15].

The focus of this study is to quantify the kinetics of cross-linking in polyisoprene by producing particles which have negligible gel content, then subjecting them to conditions under which cross-linking is significant. While natural rubber latex can provide a polyisoprene seed with comparatively low levels of cross-linking, it has a highly polydisperse particle size distribution and natural rubber also contains numerous other species (lipids, proteins, carbohydrates, and inorganic salts) that cannot be easily removed and may have significant effects. Hence, natural rubber latex does not provide a suitable substrate for the objectives of the present study, requiring synthesis of polyisoprene latexes with minimal cross-linking.

In conventional emulsion polymerizations of isoprene using thermal initiators, a certain level of cross-linking seems to be inevitable. Gel content (10–80%) is normally

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obtained and gel content increases with conversion [16]. The relative cross-linking rate for isoprene emulsion polymerization (the ratio of the cross-linking rate coefficient to the propagation rate coefficient) has been found to show a significant activation energy [16]. Maintaining the reaction temperature as low as possible will therefore minimize cross-linking, and this can be achieved by use of a redox initiation system.

### 1.1. Mechanistic precepts

It is now well established that particle formation and growth in emulsion polymerization are mechanistic events largely controlled by events in the aqueous phase [17]. The most widely accepted model for particle formation in emulsion polymerization suggests that particle nucleation above the critical micelle concentration (cmc) occurs as follows (e.g. [17]): (a) radicals are formed from initiator in the aqueous phase; (b) these radicals can propagate with monomer and/or undergo mutual termination in the aqueous phase; (c) at a critical degree of polymerization (DP)  $z$ , the oligomeric radicals become hydrophobic enough to enter monomer-swollen micelles [18]; (d) further rapid propagation of these radicals in these monomer-rich environments results in the formation of a new particle.

Initiation and particle nucleation phenomena have been studied in the emulsion polymerization of diene monomers such as butadiene, chloroprene, isoprene, and their derivatives [7,8,19–29] in the presence and absence of mercaptans. The results obtained suggest that the initiators used are inefficient in particle formation and that the oligomeric radicals predominately undergo aqueous-phase termination before reaching a DP of  $z$ .

Quantitative and qualitative understanding of emulsion polymerization systems is greatly aided by a knowledge of the propagation rate coefficient,  $k_p$ . It is now well established that the only reliable current means of determining  $k_p$  is pulsed-laser polymerization (PLP), with the raw data being required to obey various consistency criteria [30,31]. Unfortunately, there are no PLP data in the literature for isoprene. Values of  $k_p$  for butadiene (which might have a similar  $k_p$  to that of isoprene) have been reported in a single early PLP study [22], but these PLP measurements do not satisfy the IUPAC reliability criteria [30,31] established after that work appeared, and difficulties with these data have been revealed [32]. Moreover, these data give a value of  $k_p$  at 60 °C of  $2.0 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$ , contrasting with a value of  $3.2 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  inferred from emulsion polymerization wherein it appeared that the system had reached the plateau where  $\bar{n} = 1/2$ , [33], whence  $k_p$  can be inferred from the polymerization rate. Morton et al. [34] inferred values of  $k_p$  from overall polymerization rates by assuming this limiting value of  $\bar{n} = 1/2$ , but there was no reliable test of this assumption in their treatment. Indeed, their data yield an activation energy of  $41 \text{ kJ mol}^{-1}$ , whereas the highest value for an activation energy of

propagation deemed fully reliable (i.e., from consistent PLP data obtained by different groups in different laboratories) is  $32.5 \text{ kJ mol}^{-1}$  for styrene [30]. A value of  $k_p$  of isoprene (initiated by di-*t*-butyl peroxide at 5 °C) has been reported using the electron spin resonance (ESR) method [35]. However, it has been established [36] that extreme care is needed to obtain reliable  $k_p$  values using ESR, and artifacts can easily arise [36–38]. It is concluded that there are no reliable  $k_p$  data yet available for isoprene, posing a problem for mechanistic understanding; however, the PLP and emulsion polymerization data together suggest that the value of  $k_p$  is relatively low ( $2 \times 10^2$ – $3 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  at 60 °C compared to  $3.4 \times 10^2 \text{ M}^{-1} \text{ s}^{-1}$  for styrene, a monomer with a very low  $k_p$ , at the same temperature [30]).

Low yields of polyisoprene in emulsion systems thermally initiated with persulfate can be explained by two possible mechanisms: (a) directly from a possible low  $k_p$  of isoprene, giving a slow rate of polymerization in the organic phase; (b) indirectly, due to a low  $k_p$  of isoprene giving a long aqueous-phase lifetime before particle entry, and hence low entry efficiency due to termination of isoprene oligomers in the aqueous phase.

Only a few reports on the emulsion polymerizations of isoprene using redox initiators have appeared in the open literature, with relatively low yields achieved using redox couples involving cumyl hydroperoxide [39], and hydrogen peroxide and a peroxidase [40].

For redox initiation systems, the aqueous-phase and interfacial processes relevant to particle formation and growth are poorly understood. The persulfate/bisulfite redox couple (KPS/SBS) has been widely used in emulsion polymerizations [41] and is believed to generate both sulfate radical anions ( $\text{OSO}_3^-$ ) and bisulfite ( $\text{OSO}_2\text{H}$ ) radicals, either of which may initiate polymerization [42–44]. The relative effectiveness of these two radicals is not known, as chain transfer to the bisulfite anion can generate end-groups identical to those formed by addition of a bisulfite radical [45]. The *tert*-butyl hydroperoxide/tetraethylene-pentamine (*t*-BHP/TEPA) redox couple generates a single effective radical species, the *t*-butoxy radical, and has been used in the chemical modification of NRL (see Ref. [46] and references therein).

The low reactivity of the isoprene monomer leads to a high sensitivity to impurities [47] and a long period of inhibition before polymerization commences in which aqueous phase radicals derived from initiator are terminated by adventitious species. This period is significant even with rigorous exclusion of oxygen and is usually minimized by addition of a mercaptan [24]. In the thermally-initiated emulsion polymerization of isoprene and butadiene, mercaptans such as *tert*-dodecyl mercaptan (*t*-DM) have been found to be essential additives to achieve high conversion [8,26,48]. It has been suggested that the mercaptan enhances entry efficiency: through chain transfer from a sulfate or oligomeric isoprene radical to the thiol, which may enter micelles/particles directly, and/or form an entering species

after fewer propagation steps than would otherwise be the case [23]. The  $z$  value of the resulting *t*-dodecyl terminated radical is expected [49] to be very competitive with propagation due to the lower water-solubility of *t*-DM,  $3 \times 10^{-5}$  M, compared to that of isoprene,  $8.2 \times 10^{-3}$  M [50].

### 1.2. Peroxide cross-linking

The physical and chemical properties of polymers depend on the type and degree of cross-linking. Many cross-linking agents are used commercially for the vulcanization of rubber and have been extensively investigated (e.g., sulfur, tetramethylthiuram disulfide, dicumyl peroxide) [51–56]. Peroxide initiators can generate C–C cross-links, analogous to those formed in situ during a polymerization, which are of superior strength compared to the C–heteroatom bonds normally produced in vulcanization [57–63].

The mechanism of polyisoprene cross-linking with peroxide initiator has been examined by nitroxide trapping using squalene (a 30-carbon analogue of polyisoprene) [4]. In this work, benzoyl peroxide (BPO) was used as thermal initiator and TEMPO [64,65] as radical trap. The rate of abstraction by the highly reactive and electrophilic benzoyloxy radical was found to be three times larger than its addition to the internal double bonds of squalene, and the majority of addition was to terminal double bonds, suggesting that hydrogen abstraction is the dominant cross-linking mechanism when polyisoprene is treated with peroxides. Chain scission by oxidative degradation is frequently observed in polydienes exposed to oxygen [57, 66,67]. This scission can affect significantly cross-linking reaction kinetics and the final physical properties of a polymer product.

### 1.3. Methodology

The objectives of the present paper are to determine appropriate conditions for preparation of polyisoprene with low cross-link density, then to obtain quantitative abstraction rate from this system.

Both seeded and ab initio emulsion polymerizations of isoprene are carried out to separate the nucleation and particle growth processes in order to explain the previously reported low yield of polyisoprene initiated by redox systems [39,40]. Polystyrene latexes of different diameters (30, 65, and 139 nm, measured by photon correlation spectroscopy) were used as seeds, with an oil-soluble initiator couple to reduce the likelihood of secondary particle nucleation. This ‘hetero-seeded’ polymerization of isoprene in a styrene seed assumes full compatibility between the different species of polymer involved, which should be an adequate approximation at low to moderate conversion [68]. Different methods of feeding monomer/

initiator, variations in initiator concentration and in type of surfactant were also investigated.

In ab initio polymerizations, water-soluble persulfate and hydroperoxide initiators were used and the effects of these reaction variables on gel content and conversion were investigated.

A model polyisoprene latex prepared using the *tert*-butyl hydroperoxide/tetraethylene-pentamine redox couple at 25 °C was reacted with benzoyl peroxide at 70 °C. Several experiments were carried out with varying initiator concentration and volume fraction of polyisoprene. The abstraction rate was determined using  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and gel permeation chromatography (GPC).

## 2. Experimental

### 2.1. Materials

Isoprene and styrene monomers were purified using an inhibitor removal column with packings (Aldrich Catalog No. 31,134-0 for removing *t*-butylcatechol from isoprene and 31,133-2 for removing hydroquinone from styrene) and stored at  $-5$  °C until use. Potassium persulfate (KPS), cumene hydroperoxide (CHP, 80% in water), and *tert*-butyl hydroperoxide (*t*-BHP, 70% in water) were used as oxidizing agents and sodium bisulfite (SBS), *N,N*-dimethyl aniline (DMA), and tetraethylene-pentamine (TEPA) as reducing agents, without further purification. Sodium dodecyl sulfate (SDS, 99%), sodium dihexyl sulfosuccinate (Aerosol MA80), nonylphenol ethoxylate (Teric N12), and propylene oxide ethylene copolymer (Teric PE62) were used as surfactants. Sodium hydrogencarbonate, *tert*-dodecyl mercaptan (*t*-DM), and iron(II) sulfate 7-water were used without purification. Benzoyl peroxide (BPO, 75 wt% in water, Fluka Co.) was purified by recrystallization in cyclohexane and used as initiator. Toluene was used as a swelling solvent to vary the polymer volume fraction. Distilled and deionized (DI) water (Milli-Q,  $>18.2$  M $\Omega$ ) was used after 30 min degassing and 1 hr purging with nitrogen.

### 2.2. Ab initio and seeded emulsion polymerizations

In ab initio polymerizations, KPS/SBS and *t*-BHP/TEPA were used as redox couples and the oxidizing agent (KPS or *t*-BHP) was either fed continuously over the course of the reaction or added at once at the beginning. Batch reactions were done in 100 ml bottles, whose temperature was controlled by thermostat, with a magnetic stirrer. In the case of continuous feeding, reactions were carried out in a 250 ml bottom-rounded glass reactor equipped with a micro-syringe pump and mechanical stirrer, suspended in a thermostat water bath. The recipes for ab initio and seeded polymerizations are given in Tables 1 and 2, respectively.

All redox polymerizations were done at 25 °C. Several

Table 1

Recipes, gel contents, particle sizes and particle numbers for ab initio emulsion polymerizations of isoprene or styrene (molar concentrations based on amount of aqueous continuous phase)

Run	Monomer (M)	Surfactant (mM)	Initiator <sup>a</sup> (mM)	NaHCO <sub>3</sub> (mM)	<i>t</i> -DM (mM)	Temperature (°C)	Conv. (%) / time (h)	$R_{p,max}$ ( $\times 10^5$ M s <sup>-1</sup> )	Gel <sup>b</sup> (%)	Diameter <sup>b</sup> (nm)	$N_p$ (l <sup>-1</sup> )
A1	Isoprene/1.60	SDS/57.9	KPS/8.1	19.0	None	65	95/13	5.94	38	37	$4.9 \times 10^{17}$
A2	Isoprene/1.60	SDS/57.9	KPS/4.0	19.0	None	65	91/13	4.75	35	38	$4.3 \times 10^{17}$
A3	Isoprene/1.60	SDS/57.9	KPS/8.1	38.0	None	65	95/13	6.13	30	36	$5.3 \times 10^{17}$
A4	Isoprene/1.60	SDS/86.8	KPS/8.1	19.0	None	65	96/13	11.87	43	34	$6.3 \times 10^{17}$
A5	Isoprene/1.60	SDS/57.9	KPS/8.1	19.0	1.6	65	95/13	5.74	26	35	$5.8 \times 10^{17}$
A6	Isoprene/1.60	SDS/57.9	KPS/8.1	19.0	27.0	65	95/13	5.34	8	36	$5.3 \times 10^{17}$
A7	Isoprene/1.47	Aerosol MA80/41.2	KPS/14.8	None	None	60	55/39	0.48	28	102	$1.2 \times 10^{16}$
A8	Isoprene/1.47	Aerosol MA80/41.2	KPS/14.8	None	None	70	94/22	2.30	91	62	$9.4 \times 10^{16}$
A9	Styrene/0.96	Aerosol MA80/41.2	KPS/SBS/12.2	None	2.1	25	93/5	8.30	N/A	68	
A10	Styrene/0.96	Aerosol MA80/41.2	<i>t</i> -BHP/TEPA/12.2	None	2.1	25	92/5	6.50	N/A	84	
A11	Isoprene/1.47	Aerosol MA80/41.2	KPS/SBS/18.7	None	3.3	25	3/24	0.05	N/A	N/A	
A12	Isoprene/1.47	Aerosol MA80/41.2	<i>t</i> -BHP/TEPA/18.7	None	3.3	25	35/24	0.53	0	110	$6.3 \times 10^{15}$
A13	Isoprene/2.45	SDS/49.6	KPS/SBS/10.1	17.0	1.8	25	2/84	0.01	N/A	N/A	
A14	Isoprene/2.45	SDS/49.6	KPS/SBS/10.1	17.0	1.8	25	1/24	0.02	N/A	N/A	
A15	Isoprene/2.45	SDS/49.6	<i>t</i> -BHP/TEPA/10.3	19.5	2.1	25	19/24	0.36	0	36	$1.6 \times 10^{17}$
A16	Isoprene/1.47	Teric N12/52.0	<i>t</i> -BHP/TEPA/31.1	None	16.0	25	47/39	0.46	0	51	$8.5 \times 10^{16}$
A17	Isoprene/1.47	Teric PE62/13.0	<i>t</i> -BHP/TEPA/31.1	None	16.0	25	3/39	0.03	N/A	N/A	
A18	Isoprene/1.47	Teric PE62/13.0	KPS/SBS/31.1	None	16.0	25	2/39	0.02	N/A	N/A	
A19	Isoprene/1.47	Aerosol MA80/61.8	<i>t</i> -BHP/TEPA/18.6	None	4.9	25	98/39	2.50	0	60	$1.1 \times 10^{17}$
A20	Isoprene/1.47	Aerosol MA80/51.2	<i>t</i> -BHP/TEPA/18.6	None	4.9	25	91/39	1.70	0	84	$3.7 \times 10^{16}$
A21	Isoprene/1.47	Aerosol MA80/41.2	<i>t</i> -BHP/TEPA/18.6	None	4.9	25	48/39	0.45	0	105	$9.9 \times 10^{15}$
A22	Isoprene/1.47	Aerosol MA80/41.2	<i>t</i> -BHP/TEPA/18.6	None	14.8	25	55/39	0.46	0	105	$1.1 \times 10^{16}$
A23	Isoprene/1.47	Aerosol MA80/41.2	<i>t</i> -BHP/TEPA/18.6	None	None	25	43/39	0.41	8	100	$1.0 \times 10^{16}$
A24	Isoprene/1.47	Aerosol MA80/41.2	<i>t</i> -BHP/TEPA/27.9	None	4.9	25	52/39	0.46	1	101	$1.2 \times 10^{16}$
A25	Isoprene/1.47	Aerosol MA80/41.2	<i>t</i> -BHP/TEPA/11.7	None	4.9	25	37/39	0.37	0	108	$7.0 \times 10^{15}$
A26	Isoprene/1.47	Aerosol MA80/41.2	KPS/SBS/31.1	None	16.0	25	4/39	0.05	N/A	N/A	
A27	Isoprene/1.47	SDS/69.4	KPS/SBS/31.1	None	16.0	25	21/39	0.23	0	38	$9.1 \times 10^{16}$
A28	Isoprene/1.47	SDS/69.4	<i>t</i> -BHP/TEPA/31.1	None	16.0	25	85/37	1.50	1	45	$2.2 \times 10^{17}$

<sup>a</sup> A13–A15: initiator solution (KPS or *t*-BHP) was fed continuously. The initiator feeding rate was 0.002 ml min<sup>-1</sup> for A13, 0.01 ml min<sup>-1</sup> for A14 and A15. Fe(II) (0.05 mM) was added before the initiator feeding in A13 and A14.

<sup>b</sup> N/A: not available due to low conversion of isoprene.

Table 2

Recipe for seeded emulsion polymerizations of isoprene or styrene using polystyrene seed latexes at 25 °C (molar concentrations based on amount of aqueous phase)

Run	Monomer (M)	Seed latex <sup>a</sup> $D_p$ (nm)	Surfactant (mM)	Initiator <sup>b</sup> (mM)	<i>t</i> -DM (mM)	Conv. (%) / time (h)	$R_{p,max}$ ( $\times 10^{-5}$ M s <sup>-1</sup> )	Gel <sup>c</sup> (%)	Diameter <sup>c</sup> (nm)	$N_p$ (l <sup>-1</sup> )	$R_{p,max}/N_p$ ( $10^{-24}$ mol s <sup>-1</sup> )
S1	Isoprene/0.83	30	SDS/48.9	CHP/DMA/7.9	None	87/48	0.59	0	54	$3 \times 10^{18}$	2.0
S2	Isoprene/0.83	30	SDS/48.9	CHP/DMA/7.9	None	74/48	0.37	0	52	$3 \times 10^{18}$	1.2
S3	Isoprene/0.83	30	SDS/48.9	CHP/DMA/7.9	None	88/48	0.62	0	54	$3 \times 10^{18}$	2.1
S4	Isoprene/0.83	30	SDS/48.9	CHP/DMA/7.9	None	85/48	0.44	0	53	$3 \times 10^{18}$	1.5
S5	Isoprene/0.83	30	SDS/48.9	CHP/DMA/0.8	None	26/48	0.11	0	48	$3 \times 10^{18}$	0.4
S6	Isoprene/0.83	30	SDS/48.9	KPS/SBS/7.9	2.1	8/24	0.06	N/A	N/A	$3 \times 10^{18}$	0.2
S7	Isoprene/0.83	65	SDS/23.1	CHP/DMA/7.9	None	11/48	0.05	N/A	87	$3 \times 10^{17}$	1.7
S8	Isoprene/0.83	139	SDS/11.2	CHP/DMA/7.9	None	0/48	0.01	N/A	146	$3 \times 10^{16}$	3.3
S9	Styrene/0.54	139	SDS/11.2	CHP/DMA/7.9	None	8/48	0.03	N/A	149	$3 \times 10^{16}$	10.0

<sup>a</sup> 2.4 g of seed latex solid (polystyrene) was used for all seeded emulsion polymerizations.

<sup>b</sup> S6: KPS solution was fed continuously at the rate of 0.01 ml min<sup>-1</sup> in the presence of SBS and 0.05 mM of Fe(II).

<sup>c</sup> N/A: not available due to low conversion of isoprene.

ab initio polymerizations were done at 60–70 °C using KPS as thermal initiator.

In seeded polymerizations, CHP/DMA was used as the redox couple. The feeding method was varied as follows.

Run S1: polystyrene latex was swollen with CHP and isoprene initially, and then the reaction was initiated by adding DMA; run S2: polystyrene latex was swollen with CHP only and a mixture of DMA with isoprene monomer was then added; run S3: polystyrene latex was swollen with DMA and isoprene, and the reaction was initiated by adding CHP; run S4: polystyrene latex was swollen with DMA only and a mixture of isoprene and CHP was added.

Polystyrene seed latexes having different particle diameters (30, 65, and 139 nm) were dialyzed before use and SDS calculated to give 70% surface coverage based on the surface area of unswollen seed particle and area per surfactant molecule (0.42 nm<sup>2</sup> [69]) was added. Polystyrene latex of 30 nm diameter was kindly provided by BASF-AG, Germany [70], and the other polystyrene latexes were synthesized by conventional emulsion polymerization. Swelling was performed overnight at room temperature. Polymerization was initiated by injecting the oxidizing half of the redox couple with or without isoprene monomer. The saturation concentration of isoprene ( $6.4 \pm 0.1$  M) in polystyrene latex was determined by dilatometry at 25 °C [71] and an amount less than this (6.1 M) was used in order to ensure no monomer droplets were present.

The partitioning of initiator couples was not measured; however, both KPS and *t*-BHP are water-soluble (60 and 100 g l<sup>-1</sup>, respectively, at 25 °C) as are the reducing agents used in ab initio polymerizations, SBS and TEPA (> 100 g l<sup>-1</sup> at 22 °C, from pH 1–10). Thus, most initiating radicals are expected to be generated in the aqueous phase. Both CHP and DMA are only sparingly water-soluble, in the range of pH 7–10 [72], and it is assumed the majority of radicals using this redox couple are generated in the particle phase. Partition coefficients of *t*-BHP and CHP between

styrene and water have been estimated as 100 and 1000, respectively [73].

### 2.3. Characterization

Conversion data as a function of time were obtained by gravimetry. Latex sampling was done using a syringe under a positive pressure of nitrogen to ensure exclusion of oxygen. Two to three drops of hydroquinone in methanol (200 ppm) were added to each sample to ensure polymerization had ceased. Gravimetric rate data were deemed sufficient for semi-quantitative comparison between different isoprene systems and these are reported as maximum rate values. While dilatometry is more accurate for rate measurements, this technique is difficult to implement with a low-boiling monomer such as isoprene and the absence of reliable values for  $k_p$  vitiates the usefulness of accurate rate data.

The average particle size (hydrodynamic diameter, nm) was determined using photon correlation spectrometry (PCS, Brookhaven Instruments BI-200SM).

Gel content was measured by gravimetry. After inhibition of polymerization by the addition of a few drops of 200 ppm hydroquinone in methanol, surfactant and other chemicals were removed by dialysis in DI water until the conductivity of the water showed a constant value. The polyisoprene latex was then coagulated using an excess of methanol and dried under vacuum at room temperature for 2 days. The solid polyisoprene (approx. 0.1 g) so obtained was dissolved in an excess of toluene (approx. 15 g) and stirred gently for 3 days in darkness. The resulting solution was filtered using a 100 µm glass filter to separate linear and lightly branched polyisoprene from the entangled/cross-linked polyisoprene matrix in toluene. To test the reproducibility of gel content determinations, 45 and 100 µm filters and a paper filter for soxhlet extraction were tested for the filtration. Significant variation of gel content with stirring rate were found for the paper filter and it was judged that the

pore size was too large to filter swollen particles. The 45  $\mu\text{m}$  filter was too small because the gel contents varied significantly and depended on the solvent and stirring time. The 100  $\mu\text{m}$  filter was found to give reproducible results. The unfiltered and filtered portions of polyisoprene were weighed after drying.

Molecular weight distributions (MWD) were determined using GPC. Analyses were carried out using a Shimadzu GPC system fitted with a series of Waters columns (HR4, HR3 and HR2) at a temperature of 30 °C. Molecular weight was determined from refractive index data analyzed with Polymer Laboratories Cirrus™ software. The eluent was tetrahydrofuran (THF) with a flow rate of 1.0 ml min<sup>-1</sup>. Raw data were calibrated using universal calibration from styrene standards with polyisoprene Mark–Houwink–Sakurada constants  $K = 2.8 \times 10^{-4} \text{ dl g}^{-1}$  and  $a = 0.71$  [74].

The microstructure of polyisoprene prepared by *t*-BHP/TEPA at 25 °C was examined by 300 MHz <sup>1</sup>H- and <sup>13</sup>C NMR (Bruker Co.). The measurement temperature was 300.0 K and the solvent was chloroform (CDCl<sub>3</sub>). An FT-IR spectrophotometer (Perkin Elmer Co.) was used to confirm the vinyl (1,2-addition, 910 cm<sup>-1</sup>) and vinylidene (3,4-addition, 890 cm<sup>-1</sup>) structures of polyisoprene.

#### 2.4. Cross-linking protocol

Latex A28 was used as seed latex after dialyzing for 1 week under a nitrogen atmosphere. The dialysis was carried out with SDS solution at the same molar concentration as present in the seed latex to prevent coagulation. The cross-linking reaction was performed in a 60 ml double-walled jacketed reactor with a magnetic stirrer at 70 °C. Polyisoprene seed latex (18.0 g) and 22.0 g of deionized water were injected in the reactor, followed by the addition of BPO in the calculated amount of toluene (Table 3). Latex was swollen over 24 h at 20 °C with continuous nitrogen purging. The saturation concentration (6.5 M polymer at 50 °C) of toluene in polyisoprene was measured by dilatometry and this value was used for the estimation of polymer weight fraction,  $w_p$ .

Table 3

Molecular weights and polydispersity indices of polyisoprene latexes prepared using 11.7 mM of *t*-BHP/TEPA, 61.8 mM of Aerosol MA80, and 4.9 mM of *t*-DM at 25 °C

Reaction time (h)	Conversion (%)	$\bar{M}_n$ ( $\times 10^3$ )	$\bar{M}_w$ ( $\times 10^3$ )	PDI, $\bar{M}_w/\bar{M}_n$
9	47	7.6	22.5	3.0
15	61	6.8	25.0	3.6
24	82	7.2	27.0	3.7
39	92	6.2	27.1	4.4

### 3. Results and discussion

#### 3.1. Polymerization rates

Recipes and final properties for emulsion polymerization of isoprene using redox initiation with either KPS or *t*-BHP are given in Tables 1 and 2. To compare the effectiveness of redox initiations using persulfate and hydroperoxide in ‘normal’ emulsion polymerizations, emulsion polymerizations of styrene (A9, A10 in Table 1 and S9 in Table 2) were also carried out with these initiators. Fig. 1 shows representative time-conversion curves of styrene and isoprene emulsion polymerizations using redox initiations (A9–12 in Table 1) in which the same concentration of *t*-DM was added. Polymerization rates for isoprene are much slower than those of styrene for both types of initiator. Conversions of styrene were 93 and 92% within 5 h, respectively. For styrene, rates of polymerization could be converted to approximate values of the average number of radicals per particle,  $\bar{n}$ , using the well-established value of  $k_p$  for this monomer [30] and the relation:

$$R_p = -\frac{dn_M}{dt} = k_p[M]_p \bar{n} \frac{N_p}{N_A} \quad (1)$$

where  $n_M$ , number of moles of monomer per unit volume of aqueous phase,  $[M]_p$ , monomer concentration in particles,  $N_p$ , number of particles per unit volume of aqueous phase and  $N_A$ , Avogadro’s constant. Particle size (as unswollen particle radius  $r_u$ ) is trivially related to particle number by:

$$N_c = \frac{m_p}{\frac{4}{3}\pi r_u^3 d_p} \quad (2)$$

where  $m_p$ , initial mass of polymer (as dried weight of seed

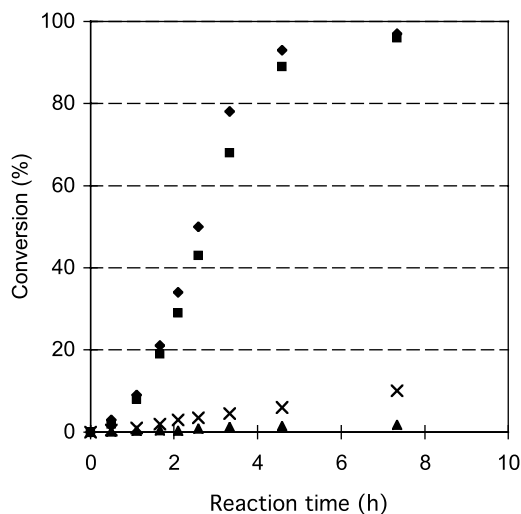


Fig. 1. Representative time-conversion curves of emulsion polymerizations using redox initiators: (◆) A9, KPS/SBS with styrene; (■) A10, *t*-BHP/TEPA with styrene; (▲) A11, KPS/SBS with isoprene; (×) A12, *t*-BHP/TEPA with isoprene. Details listed in Table 1.

latex) per unit volume of the aqueous phase and  $d_p$ , density of polymer.

The maximum polymerization rate for each polymerization,  $R_{p,max}$ , was calculated from the first derivative of a third order polynomial fitted to the time-conversion data (Tables 1 and 2). The  $R_{p,max}$  values from persulfate-initiated and hydroperoxide-initiated polymerizations of styrene showed no significant difference. This is consistent with a system following conventional zero-one kinetics [17] with  $\bar{n} \sim 0.5$ , as expected for small particles with high radical flux. (Values of  $\bar{n}$  in A9 and A10 were determined to be 0.49 and 0.41, respectively. As  $\bar{n}$  is sensitive to small errors in the measured particle size, it is reasonable to assume that the true values are in fact very close to 0.5). The similarity with rate for the two initiators suggested that both behave as expected in a conventional emulsion polymerization. In the polymerizations of isoprene, however, the  $R_{p,max}$  for the KPS/SBS couple was smaller than that of the hydroperoxide by an order of magnitude, and two orders of magnitude smaller than the styrene polymerization rates. The yields of polyisoprene for most persulfate-initiated redox systems are very low (<10% for 48 h at 25 °C). This cannot be explained in terms of an innate low  $k_p$  of isoprene, since hydroperoxide-initiated polymerizations showed a reasonable  $R_{p,max}$ . Conversely, most *t*-BHP/TEPA initiation systems showed satisfactory yields at reasonably high concentrations of surfactant. This can be explained by noting that the primary radicals or oligomeric radicals from *t*-BHP are more lipophilic than persulfate-initiated radicals and may more easily enter micelles or particles. Note from Fig. 1 that although the initiator was added as a single aliquot at the beginning of the reaction, the reaction appears to proceed at a steady rate towards full conversion, suggesting the rate of initiator consumption is slow.

### 3.2. *Ab initio* polymerizations

Inspection of the conversion-time data and  $R_{p,max}$  of *ab initio* polymerizations shows that the polymerization rate is significantly affected by the type of initiator. The KPS/SBS redox couple gave neither high conversions nor reproducible results regardless of type and concentration of surfactants (A11, 13, 14, 18, 26 and 27 in Table 1). This result was also seen in seeded emulsion polymerizations. It is possible that the reaction between KPS and SBS is complete in a very short time. Because of this, some runs were conducted with continuous feed of initiator; however, no significant difference in reaction rate or products formed was found over a range of feed rates (runs A13–A15 in Table 1). The large differences in  $R_{p,max}$  imply that *t*-BHP is a much more efficient initiator than KPS, although the entry mechanism is not clear: *t*-butoxy primary radicals, on their own, may be hydrophobic enough to enter the monomer-rich micelles or the *t*-butoxy radical may give oligomeric radicals with a reduced  $z$  value.

Butadiene monomer can be expected to show similar

behavior to isoprene, and for butadiene polymerization initiated by KPS,  $z$  has been estimated to be 3, with a calculated entry efficiency of 4% at 50 °C [17]. We can estimate the length of the  $z$ -mer for persulfate-initiated radicals in isoprene/KPS using [18]:

$$z \approx 1 + \frac{23 \text{ kJ mol}^{-1}}{RT \ln([M]_w^{\text{sat}}/M)} \quad (3)$$

where  $[M]_w^{\text{sat}}$  is the saturated concentration of monomer in water. The  $z$  value for isoprene ( $[M]_w^{\text{sat}} = 8.2 \text{ mM}$  at 25 °C) is thus calculated as 3, compared to  $z = 2$  for styrene at the same temperature. The value of  $z$  then dictates the initiator efficiency [18]:

$$f = \left\{ \frac{(k_d[I]k_{t,aq})^{1/2}}{k_{p,aq}[M]_w} + 1 \right\}^{1-z} \quad (4)$$

where  $k_d$ , initiator dissociation rate coefficient,  $k_{t,aq}$ , aqueous-phase termination rate coefficient of all radicals, and  $k_{p,aq}$ , aqueous-phase propagation rate coefficient. As stated, the value of the propagation rate coefficient is not known with any certainty. However, if one assumes that  $k_p$  for polyisoprene is relatively low (which is consistent with the various values discussed above), then the fact that its value of  $z$  is higher than styrene, which also has a low  $k_p$ , while their water solubilities are similar, suggests that the entry efficiency for isoprene could also be low. However, this inference is by no means rigorous.

It was observed that the polymerization rate increased as the concentration of *t*-DM increased; however, there was no strong retardation or inhibition in the absence of *t*-DM. This is in contrast to the promoting effect of *t*-DM found by Weerts et al. [24], who reported a significant increase in conversion of isoprene-KPS emulsion polymerization when *t*-DM was used at 67 °C. This discrepancy is probably due to differences in the concentrations of initiator: 0.13 mM KPS in Weerts compared to 4–15 mM here. Results indicating no inhibition in the absence of *t*-DM have previously been described for  $[KPS] > 10 \text{ mM}$  [26].

The effects of surfactant type were not investigated systematically. It is suggested that the sensitivity to surfactant type of polymerization rate of isoprene in this work arises from the well-understood [17] dependence of rate on particle number.

### 3.3. Seeded emulsion polymerizations

Fig. 2 shows the time-conversion curves of seeded emulsion polymerizations at 25 °C, with initiation by the CHP/DMA redox couple.

The effect of seed particle size can be explained in terms of the number of polymerizing loci. While values of  $\bar{n}$  (average number of radicals per particle) cannot be determined because no reliable values of  $k_p$  are available, one can determine the (maximum) rate per particle, which is proportional to  $\bar{n}$ ; these values are given in Table 2 as

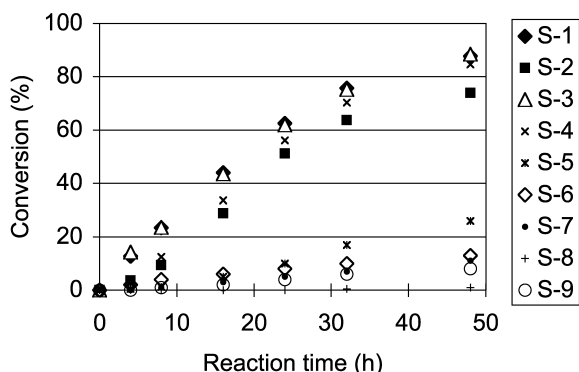


Fig. 2. Time-conversion curves for seeded emulsion polymerizations in polystyrene seed latexes. Details listed in Table 2.

$R_{p,max}/N_p$ . The maximum rate per particle for all runs with  $CHP/DMA = 7.9$  mM and isoprene monomer may be meaningfully compared. The maximum rates per particle for all smaller particles (S1–S4, with seed diameter 30 nm, S7 with seed diameter 65 nm) range from  $1.5 \times 10^{-24}$  to  $2.1 \times 10^{-24}$  mol s $^{-1}$ , while that for S8 (seed diameter 139 nm) is  $3.3 \times 10^{-24}$  mol s $^{-1}$ . It is not unreasonable to assume, for well-known reasons based on the Smith–Ewart mechanism [17], that the smaller particles follow zero-one kinetics, which confines  $\bar{n}$  to values  $\leq 0.5$ , while the larger particle may have a much larger value of  $\bar{n}$  and hence higher rate per particle.

Several bulk polymerizations of isoprene were carried out using CHP/DMA under the same reaction condition as seeded polymerization but no polymer was detected after 72 h reaction. This suggests compartmentalization (isolation of radicals from each other in small particles reducing the termination rate) favors polymerization.

For the redox initiation system of benzoyl peroxide using DMA, it has been suggested that a DMA-derived radical should not initiate polymerization [75–77]. This radical is stabilized by resonance and will undergo termination and recombination reactions. It is expected, however, that the radical formed from CHP can initiate polymerization. It was observed that the color of all latexes prepared with DMA became bluish-violet, previously observed in DMA-initiated polymerizations and ascribed to the product from the recombination of DMA radicals [75,77]. The KPS/SBS redox couple was also used in seeded polymerization (S6 in Table 2), by continuous addition of KPS solution at 0.01 ml min $^{-1}$ . Conversion of isoprene monomer was low: 8% over 24 h, similar to that obtained for the ab initio polymerization.

### 3.4. Gel content

Gel contents in all seeded polymerizations initiated by CHP/DMA were found to be less than 1%. For ab initio polymerizations A1–A6, the concentration of KPS was from 4.0 to 8.1 mM and conversions of isoprene reached over 90% within 13 h at 65 °C regardless of *t*-DM dosing.

Gel contents in the present thermal-KPS runs without mercaptan were from 26 to 43%, while 8% gel content was obtained when 27 mM of *t*-DM was added.

In Fig. 3, gel content as a function of *t*-DM concentration is plotted for several thermal and redox emulsion polymerizations of isoprene. Gel content decreased as *t*-DM concentration increased. The gel contents measured in redox initiation systems were negligible even at 60% conversion and appeared to be significantly lower than for aqueous-phase initiation systems under all conditions. This can be attributed to the lower temperatures employed, as the gel content increased as the polymerization temperature increased, although the figures are not strictly comparable due to differing conversions. This behavior is as expected, as the relative activation energies of cross-linking and propagation would be expected to lead to more cross-linking at elevated temperatures. Gel content also increases with conversion, which is readily explicable in terms of the higher polymer:monomer ratio at high conversion.

### 3.5. Molecular weight distributions

The MWD of A19 as a function of conversion (Fig. 4) indicates two overlapping peaks. As the conversion increased, the signal intensity increased at both the high and low molecular weight ends of the range, broadening the distribution. This is a general effect as can be seen from Table 4 in which the number- and weight-average molecular weights,  $\bar{M}_n$  and  $\bar{M}_w$ , and polydispersity indices ( $PDI = \bar{M}_w/\bar{M}_n$ ) of polyisoprene, prepared using *t*-BHP/TEPA at 25 °C, are given as functions of conversion. It was observed that  $\bar{M}_w$  increased as the conversion increased, while  $\bar{M}_n$  showed no significant variation within experimental scatter. Increases in the low molecular weight peak as a function of conversion might be attributable to a transfer reaction to

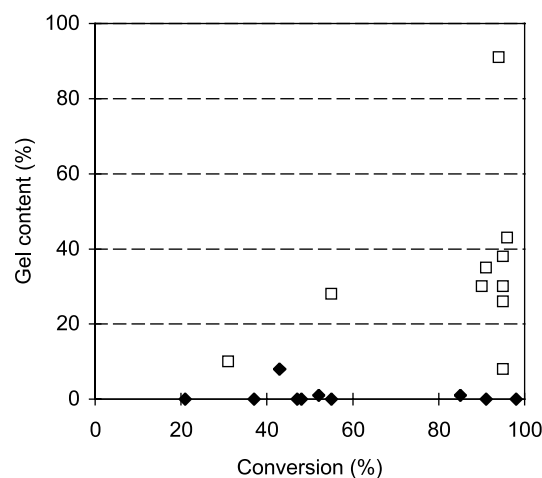


Fig. 3. Percentage gel content vs. *t*-DM concentration with varying polymerization temperature in polyisoprene latexes prepared by emulsion polymerizations initiated by thermal and redox initiations: (□) thermal initiations of KPS at 60, 65, and 70 °C (A1–A8); (◆) redox initiations of *t*-BHP/TEPA at 25 °C (A11–A12, A14–A16, A19–A25, A28).



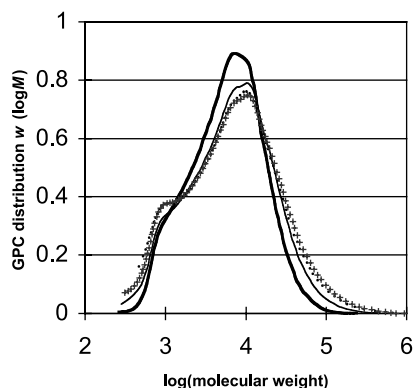


Fig. 4. Molecular weight distributions of polyisoprene A19 prepared using 11.7 mM of *t*-BHP/TEPA, 62 mM of Aerosol MA80, and 4.9 mM of *t*-DM at 25 °C: (—) 47%; (---) 61%; (•••) 82%; (+++) 92% conversions of isoprene monomer.

monomer or chain scission during the reaction as often seen in polyisoprene in the presence of hydroperoxides. Abstraction reactions leading to grafting and cross-linking can also explain the increase in the high molecular weight region.

Latex A28, a latex with negligible gel content, was chosen for further investigation. The average particle diameter by light scattering was 44 nm.  $\bar{M}_n$  and  $\bar{M}_w$  were  $10.6 \times 10^3$  and  $30.6 \times 10^3$ , respectively. The microstructure and NMR spectra are given in Fig. 5. In Fig. 5(a), sharp signals from methyl proton of *cis*-1,4 unit (j) and *trans*-1,4 (d) were observed at 1.68 and 1.58 ppm, respectively. The peaks above 4.50 ppm indicate olefinic protons of 3,4-addition (4.61–4.78 ppm), 1,2- addition (4.80–4.95 ppm), *cis*- and *trans*-1,4 (5.12–5.22 ppm), and 1,2- addition (5.71–5.78 ppm). It was found that the polyisoprene latex prepared using *t*-BHP/TEPA at 25 °C consists of 69.7% of 1,4-*trans*, 20.0% of 1,4-*cis*, 5.0% of 1,2-addition, and 5.3% of 3,4-addition structures. These figures were broadly confirmed by FT-IR. In the FT-IR spectrum, absorption bands at 838, 888, and 910  $\text{cm}^{-1}$  are characteristic of *cis*-1,4, 3,4-addition, and 1,2-addition, respectively. It was observed that *trans*-*trans* (39.8 ppm) structure was predominant and *trans*-*cis* (40.2 and 32.2 ppm) or *cis*-*cis* (32.9 ppm) structures were found to be negligible (Fig. 5(b)). No structures indicative of branch points were found by  $^1\text{H}$  NMR.

A combination of chain scission and cross-linking under radical flux is the most likely explanation for the broadening of the MWD seen in seed preparation, as a similar trend was

seen when latex A28 was treated with BPO in the absence of any monomer. Representative time-evolution of average molecular weights of run A (in Table 4) is given in Fig. 6. Both  $\bar{M}_n$  and  $\bar{M}_w$  initially decrease and increase again after 1.5 h. In particular, the  $\bar{M}_w$  increases significantly thereafter with a subsequently large polydispersity index. Similar behavior was observed in all other samples. This result implies that the chain scission reaction is dominant initially, whereas cross-linking continues throughout treatment with benzoyloxy radicals. In this study,  $\bar{M}_n$  and  $\bar{M}_w$  of polyisoprene at 0.5 h were  $12 \times 10^3$  and  $30 \times 10^3$ , respectively, which indicates negligibly small changes in the average molecular weights compared with those of polyisoprene seed particle.

In Fig. 7, MWD of run A are given as a function of reaction time. While the MWD at 0.5 h was the same as that of the seed particle, the MWD at 1.5 h shows broadening and a large increase in signal in the low MW region, suggesting chain scission. The MWD at 3.0, 7.0, and 24.0 h show little change in the low MW region, while a marked and continuing increase is seen in the high MW region. It is reasonable to infer that oxidative chain scission occurs rapidly early in the reaction, when molecular oxygen is present, while the cross-linking reaction becomes important at later stages of the overall reaction.

### 3.6. Oxidation and cross-linking reactions

In Fig. 8, the fractional change in the methylene proton signal ( $-\text{CH}_2-$ , 1.85–2.20 ppm) obtained from  $^1\text{H}$  NMR is given for runs A–D in Table 3. The initial steep slope of each curve is most likely a result of oxidative chain scission (0–1.5 h). After this time, there is a fairly constant rate of reaction with any decrease consistent with the declining concentration of BPO.

The reaction mechanism suggested for this system, given in Fig. 9, can be applied in the presence of oxygen. The benzoyloxy radical (R) formed thermally from BPO initiator abstracts hydrogen from polyisoprene, forming the polyisoprene radical. Any phenyl radicals (Ph) formed via beta-scission of the benzoyloxy radical may also abstract hydrogen. The relatively unreactive polyisoprene radical will then most likely add oxygen, yielding a peroxide radical. This radical also can abstract hydrogen to form a hydroperoxide (POOH). Oxidative chain scission occurs via an OH radical, when POOH splits to give a hydroxyl radical and a polymeric alkoxy radical which then undergoes beta-scission to cut the chain, generating a terminal aldehyde functionality and a carbon-centered radical [66,67]. Direct attack of the benzoyloxy radical on polyisoprene cannot cause chain scission (i.e. in the absence of oxygen, chain scission will be greatly diminished [78,79]). However, this mechanism does not directly explain the reduced overall rate of loss of methylene protons in the absence of oxygen. One possibility is that a substantial proportion of polyisoprene radicals formed by abstraction must re-abstract

Table 4  
Recipe for cross-linking reaction of polyisoprene at 70 °C

Run	Temperature (°C)	BPO (g)	Seed (g) <sup>a</sup>	Toluene (g)	$w_p$
A	70	0.10	18.0	0.79	0.61
B	70	0.01	18.0	3.10	0.29
C	70	0.01	18.0	0.79	0.61
D	70	0.10	18.0	0.06	0.95

<sup>a</sup> Solid content of seed latex is 0.075% (w/w).

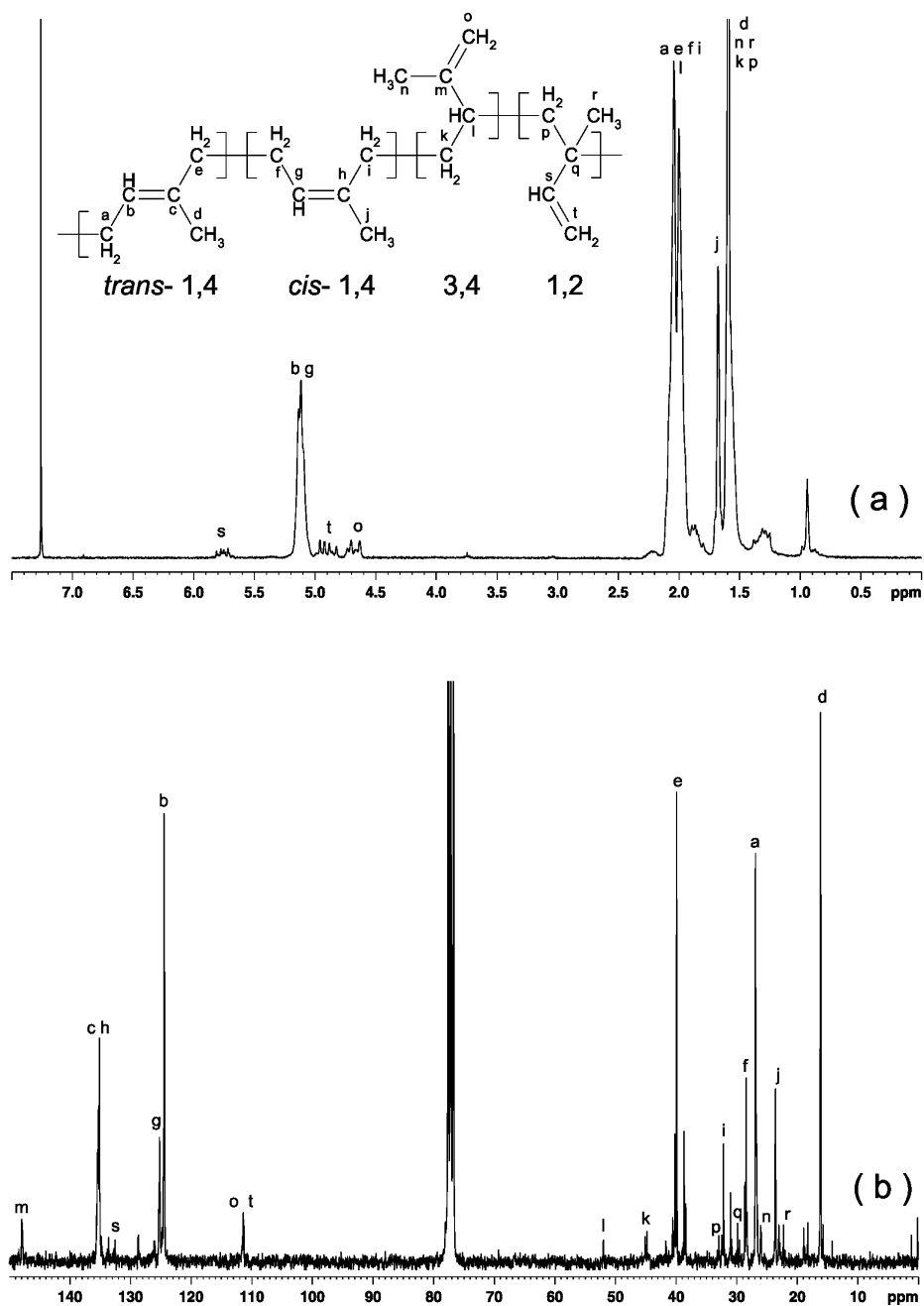


Fig. 5. (a) Microstructure and <sup>1</sup>H NMR spectrum of polyisoprene in CDCl<sub>3</sub>; (b) <sup>13</sup>C NMR of polyisoprene in CDCl<sub>3</sub>.

protons from the solvent to generate small radical species which terminate. Another is the possibility that the ROO or PhOO radicals are significantly more effective in abstraction reactions and less susceptible to termination than their parent radicals.

The cross-linking reaction in polyisoprene is achieved by the mutual termination between two polymer radicals formed by hydrogen abstraction. In the presence of oxygen, the concentration of these carbon-centred radicals will remain low, explaining the small change in the high MW range of the MWD early in the reaction. From the relative <sup>1</sup>H NMR peak areas, no change of double bonds in *cis*- or

*trans*-1,4, 1,2, and 3,4 units was observed during the cross-linking reaction. This indicates that the radicals generated do not directly attack double bond to a significant degree.

The diffusion of the BPO-derived radicals is unlikely to be significantly affected by network formation due to cross-linking reaction since polyisoprene was diluted by toluene ( $w_p = 0.29\text{--}0.95$ ) and polyisoprene itself is very rubbery at 70 °C. On the other hand, the mobility of the polyisoprene radical is expected to be strongly dependent on temperature and on  $w_p$ . If the observed methylene abstraction is dependent on the competition between this  $w_p$ -dependent diffusion and the futile regeneration of polyisoprene by

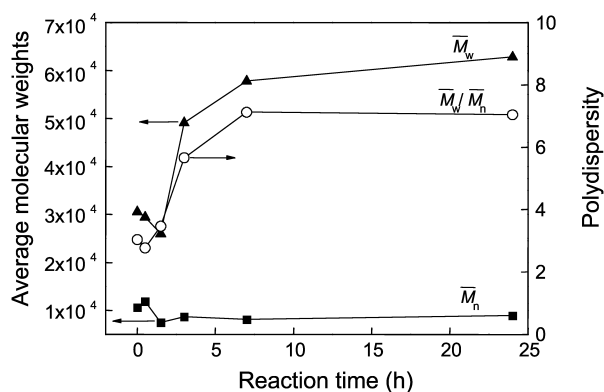


Fig. 6. The average molecular weights of run A as a function of time; run details given in Table 3.

hydrogen abstraction of backbone radicals, a consistent kinetic interpretation of the data may not be possible.

An estimate of the dependence of  $d[\text{CH}_2]/dt$  can be made by using the steady state approximation. First, it is assumed that the main fate of BPO-derived radicals is recombination with a rate coefficient  $k_t$  to give a rate proportional to  $k_t^{1/2} [\text{BPO}]^{1/2}$ . Plotting overall rates of reaction after the initial period of chain scission (Table 5) as a function of simple combinations of  $[\text{BPO}]$ ,  $[\text{CH}_2]$ , and  $w_p$  gives a very poor fit for all combinations tried ( $R^2 < 0.65$ ). However, all  $d[\text{CH}_2]/dt$  data points in the rubbery regime ( $w_p \leq 0.61$ ) lie on a straight line when plotted against  $[\text{BPO}]^{1/2} [\text{CH}_2]$  (Fig. 10). Introducing any inverse dependence of  $d[\text{CH}_2]/dt$  on  $w_p$ , as seems reasonable from the mechanism discussed above, appears to reduce both the goodness of fit and the initiator-independent rate (shown in Fig. 10 by plotting  $K[\text{BPO}]^{1/2} [\text{CH}_2]$ , where  $K = 1$  or  $w_p$ ), although this conclusion is not definite because of the paucity of data.

If it is assumed that these radicals then react to give polyisoprene radicals at a rate  $k_a[\text{R}][\text{CH}_2]$ , and that conditions are such that these polymeric radicals recombine quantitatively, the appropriate dependence is extracted. It would appear then that the simplest explanation for the

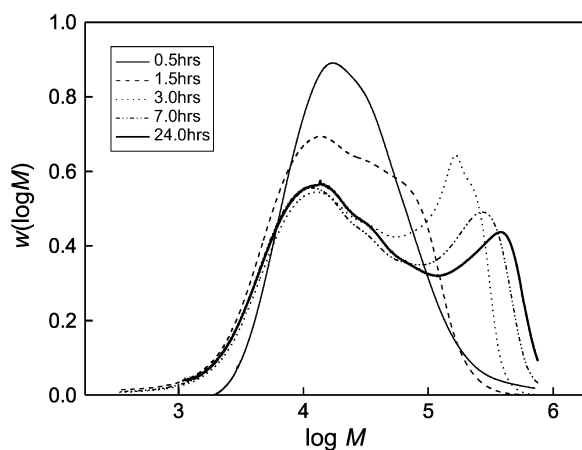


Fig. 7. Molecular weight distributions,  $w(\log M)$ , of run A as a function of time; run details given in Table 3.

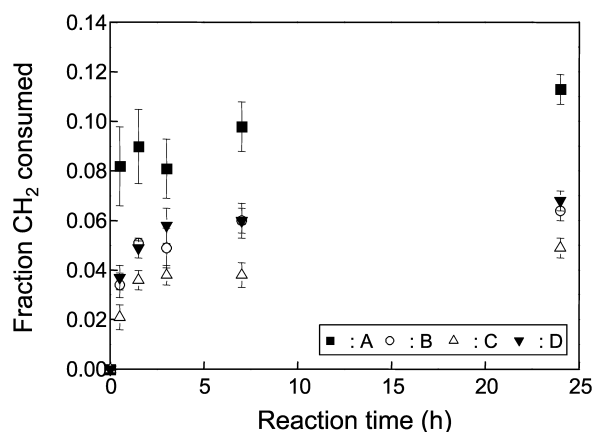


Fig. 8. Fractional changes of methylene ( $-\text{CH}_2-$ ) group during the cross-linking reactions for runs A–D; run details given in Table 3.

change in rate between the ‘oxidative scission’ region is the greater abstraction capacity of the ROO or PhOO radicals, as the ‘futile regeneration’ explanation would imply a degree of  $w_p$  dependence. Given the paucity of the data, however, it is not possible to discount the possibility of such a dependence. It is certain that a competition between bimolecular diffusion and other termination events is required to explain the high  $w_p$  (0.95) data.

#### 4. Conclusions

Ab initio and seeded emulsion polymerizations of isoprene using redox initiator couples (KPS and *t*-BHP) were investigated for the preparation of polyisoprene latexes with high yield and low gel fraction. The following mechanistic deductions are consistent with the observed rate behavior of seeded and of ab initio polymerizations.

Persulfate redox initiation is ineffective for the emulsion polymerization of isoprene. The ionic nature of persulfate initiator makes radicals formed from KPS more hydrophilic and hence  $z$ , the chain length required for surface-activity (and hence radical entry into particles for particle growth and entry into micelles for micellar nucleation), is greater than that for styrene due to the higher water solubility of isoprene. The hydrophilicity of the oligomeric radicals and the probable slow propagation rate coefficient of isoprene monomer mean that immature oligomeric radicals are more likely to terminate in the aqueous phase before entering particles.

Table 5  
Estimation of hydrogen abstraction rates of polyisoprene from  $^1\text{H}$  NMR

Run	$d[\text{CH}_2]/dt$ ( $\times 10^6 \text{ M s}^{-1}$ )	$w_p$	$[\text{BPO}]_0$ (M)	$[\text{CH}_2]_0$ (M)
A	5.16	0.61	0.167	14.56
B	1.23	0.29	0.00810	7.079
C	2.39	0.61	0.0171	14.97
D	4.00	0.95	0.253	22.15

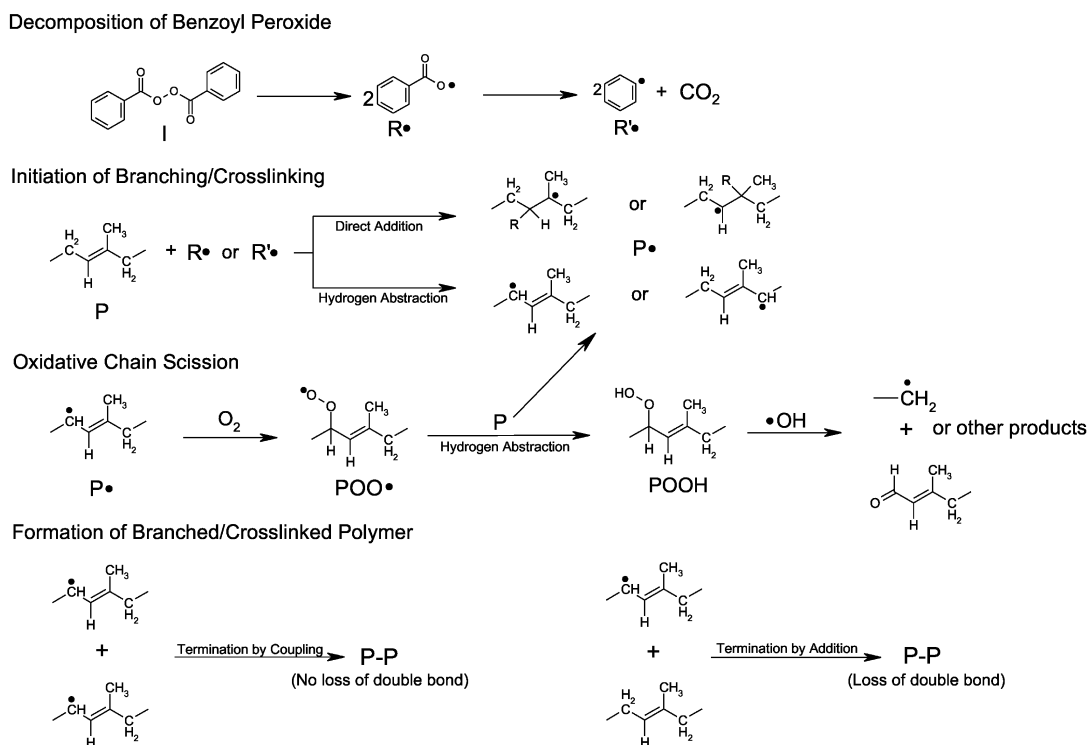


Fig. 9. Overall reaction scheme of the polyisoprene/benzoyl peroxide cross-linking process.

Hydroperoxide initiation gave relatively high polymer yield in both ab initio and seeded systems. The lipophilic properties of the hydroperoxide primary radical seem to make radical entry more favorable than in the persulfate system: the entering radical from the peroxide system is probably still surface active but with an HLB (hydrophile–lipophile balance) which favors entry. Addition of *t*-DM increased the polymerization rate in the hydroperoxide redox initiation system, as also observed in thermal initiation using persulfate, but no drastic promoting effect was observed.

Polyisoprene latexes with negligible gel content (suggesting a very low rate of cross-linking) were success-

fully synthesized; it is noted that low gel content does not imply unbranched polymer. Low gel could be achieved at room temperature only in the presence of chain transfer agent, *t*-DM, which can be ascribed to reduction in molecular weight. The MWD obtained became broader at high conversions, attributed to abstraction events leading to grafting, cross-linking, and chain scission.

Investigation of the reaction between polyisoprene and BPO in the absence of monomer showed that oxidative chain scission accelerated by BPO is dominant at the initial stage of reaction where molecular oxygen is expected to be present. Oxidative chain scission leads to formation of low molecular weight polyisoprene observed by GPC. Cross-linking reactions become predominant at intermediate and later stages of the reaction, giving an increasing proportion of high MW polyisoprene. Hydrogen abstraction rates calculated from the consumption of methylene protons at these stages of reaction implies that the hydrogen abstraction rate at low  $w_p$  is dependent on the product  $[BPO]^{1/2}[CH_2]$ , consistent with abstraction by a population of initiator-derived radicals whose primary fate is bimolecular termination. The results are consistent with a large amount of futile small-radical termination and a cross-linking rate controlled by the mutual diffusion of large polyisoprene radicals. The differences in rate in the chain-scission and cross-linking regimes may be attributable to a higher rate of abstraction for the peroxy radicals generated by attack of initiator-derived radicals on oxygen, although a  $w_p$ -dependent mechanism masked by the paucity of the data cannot be discounted.

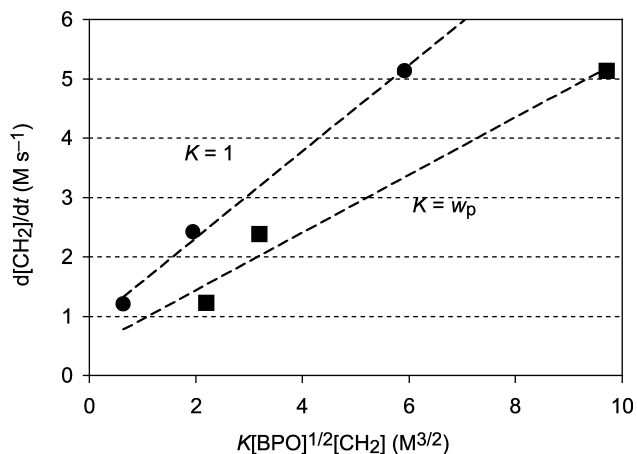


Fig. 10. Dependence of rate of methylene consumption on initial [BPO] and  $[CH_2]$ .

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