

Retardative chain transfer in free radical free-radical polymerisations of vinyl *neo*-decanoate in low molecular weight polyisoprene and toluene

M.J. Monteiro¹, N. Subramaniam², J.R. Taylor, B.T.T. Pham, M.P. Tonge, R.G. Gilbert*

Key Centre for Polymer Colloids, School of Chemistry, University of Sydney, Sydney, NSW 2006, Australia

Received 10 July 2000; received in revised form 10 October 2000; accepted 24 October 2000

Abstract

The kinetics of free-radical polymerisation of vinyl *neo*-decanoate (*VneoD*) and the molecular weight distributions (MWDs) of the polymers formed in the presence and absence of low molecular weight polyisoprene at 50°C under a variety of conditions were investigated. The bulk reaction was successfully modelled using conventional free-radical polymerisation with termination rate coefficients calculated from diffusion theory. The reaction was strongly retarded by the presence of toluene or low-molecular-weight polyisoprene. This retardation behaviour was consistent with a mechanism comprising chain transfer of the radical activity to a double bond on the polyisoprene backbone to form a radical centre of low reactivity, which may subsequently terminate with other propagating radicals (“transfer-induced retardation”). Analysis of the rate and of the MWDs of the polymer formed yielded an estimation of the rate coefficient for transfer of the radical activity from the propagating *VneoD* radical to toluene and to polyisoprene. The rate coefficients for transfer to toluene determined by both methods were similar ($7.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from the conversion-time data, and $10.8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from the molecular weight distribution). The rate coefficient for transfer to toluene was similar for both vinyl acetate ($9.9 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$) and *VneoD*, as expected given the similar radical reactivity of these monomers. The rate coefficient for transfer to polyisoprene was found by the conversion-time method to be $150 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, suggesting that the polymerisation of *VneoD* in the presence of polyisoprene would be a useful method for inducing grafts onto the polyisoprene backbone. The rate coefficients and inferred mechanism are similar to those found previously for a *VneoD*/polybutadiene system [Macromolecules, 33 (2000) 2383]. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Grafting; Polyisoprene; Retardative chain transfer

1. Introduction

There are currently two methods by which grafting may be induced in polyalkenylenes such as polyisoprene. The first is through graft-site initiation [1], where the initiator-derived radicals either add across the double bond or abstract hydrogens from the polyisoprene backbone [2]. High levels of grafting with *cis*-polyisoprene have been found to be induced with benzoyl peroxide [3] and other oxyl radicals [4], whilst azobisisobutyronitrile (AIBN) was shown to have little effect [5]. The second method is through hydrogen abstraction from polyisoprene by polymeric radicals [6]. Scanlan et al. [6,7] found that the rate was retarded in the polymerisation of vinyl acetate (VAc) in the presence

of either natural rubber, high molecular weight synthetic polyisoprene or a model compound of polyisoprene (2,6-dimethylocta-2,6-diene). However, the authors could not distinguish between retardation due to chain transfer and retardation due to copolymerisation (i.e. addition across the double bonds of polyisoprene). The chain-transfer mechanism for the observed retardation was tested by Scanlan et al. by polymerising VAc in the presence of a model compound, isopropylbenzene [7]; chain transfer is the only possible reaction in this system. Retardative chain transfer was found to occur, where the polyVAc radicals readily abstract hydrogens from isopropylbenzene, and these incipient isopropylbenzyl radicals are very unreactive towards VAc and consequently may act as primary radical terminators for polymeric radicals. This result supports the hypothesis that retardative chain transfer frequently occurs for the VAc/polyisoprene system, and therefore will invariably lead to grafting of polyVAc onto the backbone of polyisoprene.

Lehrle and Willis [8] proposed that VAc could facilitate grafting of methyl methacrylate (MMA) onto natural rubber

* Corresponding author. Fax: +61-2-9351-8651.

E-mail address: gilbert@chem.usyd.edu.au (R.G. Gilbert).

¹ Present address: Department of Polymer Chemistry and Coating Technology, Eindhoven University of Technology, P.O. Box 513, 5600 MB Eindhoven, The Netherlands.

² Present address: BASF AG, Business Unit Paper Chemicals Europe, EDP/M - H201, 67056 Ludwigshafen, Germany.

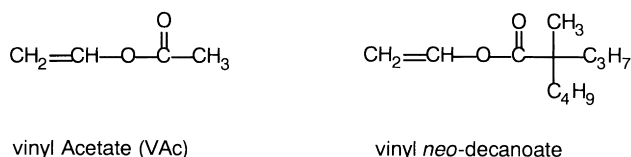


Fig. 1. Chemical structures of VAc and VneoD. VneoD is actually a mixture of branched isomers such as vinyl 2-ethyl-2-propylpentanoate, one of which is shown in the figure.

latex particles in a second-stage (seeded) emulsion polymerisation. However, their investigations showed that although grafting increased under the experimental conditions, the amount was not significant. It was proposed that this was because the oil-soluble initiator (AIBN) was not accessible to the large amounts of VAc present in the aqueous phase. Because the aqueous phase saturation concentration of VAc [9,10] is approximately five times greater than that for MMA [11], then inside the latex particles there is a lower relative concentration of VAc compared with MMA and consequently there is a lower proportion of poly(VAc) radicals available to abstract hydrogens from polyisoprene. This problem can be overcome [12,13] by using a monomer that is extremely water-insoluble and with a similar free-radical chemistry to VAc. One such monomer is vinyl *neo*-decanoate (VneoD, which is actually a mixture of branched isomers such as vinyl 2-ethyl-2-propylpentanoate), Fig. 1, which has a water solubility $\sim 10^3$ times lower than that of VAc and a chemical structure that differs only by a C_9H_{19} alkyl group. Indeed, it is likely that these two vinyl esters have very similar free-radical chemistry, as evidenced by the similarity of the frequency factor and activation energy of the propagation rate coefficient [14]. VneoD should therefore not only promote higher levels of grafts spread homogeneously throughout the natural rubber particles both in homo- and copolymerisations, but should also [12,13] decrease the probability of secondary particle formation.

Previous kinetic studies [15] have suggested that this mechanism should be very effective in inducing grafting onto polybutadiene; the present paper explores the applicability of this to polyisoprene. The objectives are: (a) to confirm that VneoD has similar grafting kinetics with polyisoprene to that observed with polybutadiene; (b) to confirm VneoD has a similar free-radical chemistry to VAc when polymerised in the presence of low molecular weight polyisoprene (LMPI); and (c) to obtain transfer rate coefficients for abstraction of hydrogens from the polyisoprene backbone by polymeric VneoD radicals. The investigations involve bulk and solution polymerisations of monomers in the presence of low molecular weight synthetic polyisoprene (a low molecular weight being necessary because samples of this polymer prepared by free-radical polymerisation with high molecular weights tend to have very high gel fractions and thus will swell with, rather than dissolving in, VneoD monomer). The retardation effect from the

presence of polyisoprene, which would arise from the low reactivity to vinyl ester monomers of allylic radicals formed by abstraction on polyisoprene, will also be compared to that found in the presence of toluene, which should exhibit an analogous retardation through the resulting benzylic radicals. Kinetic analysis will be through both rates and molecular weight distributions (MWDs) [15].

Mechanistic information from this study has the potential to lead to “designer” latexes by controlling the amount of grafting and consequently the resulting morphology of the latex particles in seeded emulsion polymerisations [12,13,16].

2. Experimental

VneoD (“VeoVa” from Shell Chemicals) was purified by two different methods. In the first method VneoD monomer was thoroughly mixed with basic alumina before pouring through a column containing fresh basic alumina. In the second method, VneoD was passed through a column containing basic alumina and then distilled under reduced pressure. The purity was analysed by GCMS (Hewlett Packard 5989A Mass Spectrometer, together with a Hewlett Packard 5890 series II Gas Chromatograph) to test for the presence of residual inhibitor. AIBN was used as initiator in this work to exclude any complications from grafting induced by the initiator-derived radicals, since [5] it has been shown not to induce significant grafting in polyisoprene.

2.1. General procedure for bulk polymerisations

In a typical bulk polymerisation, monomer was weighed into a 50 ml round-bottom flask. The *freeze-pump-thaw* technique was used to remove oxygen from the reaction mixture, and repeated three times to ensure most of the oxygen was removed prior to the polymerisation. AIBN was added into the round-bottom flask under a nitrogen atmosphere and allowed to dissolve before being immersed into an oil bath at 50°C. The amounts of monomer and initiator used were such that the final concentrations were 4.45 and 0.01 M, respectively. Conversion-time data were measured by withdrawal of samples at fixed intervals for gravimetric analysis. In the case of solution polymerisations of VneoD in the presence of toluene, a similar experimental procedure to that described above was utilised. In some bulk experiments, the conversion-time data were monitored by dilatometry for a more accurate analysis of the rate.

2.2. Preparation of low molecular weight polyisoprene

Isoprene monomer (Aldrich) was passed through a column containing basic alumina to remove inhibitor. Isoprene monomer and benzoyl peroxide were transferred into a pressure sealed vessel, containing toluene. The concentrations on mixing were 6.52, 0.19 and 3.02 M,

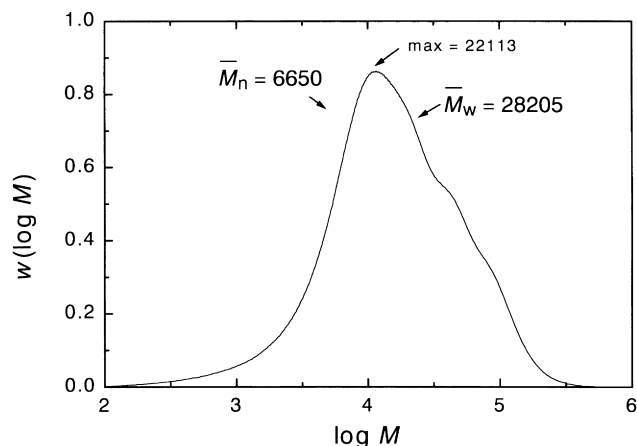


Fig. 2. GPC molecular weight distribution of LMPI polymerised from isoprene, benzoyl peroxide and toluene at 78°C.

respectively. The vessel was degassed, sealed, and placed in a water bath at 78°C. The polymerisations were allowed to proceed for 48 h. The polymer from the reaction mixture was precipitated by addition to methanol and then dried in a vacuum oven at 40°C for 48 h. The LMPI was characterised by NMR and GPC.

2.3. Polymerisation of *VneoD* with low molecular weight polyisoprene

The polymerisation of *VneoD* was carried out in the presence of LMPI initiated with AIBN. LMPI was initially dissolved in an excess of monomer. The resulting solution was filtered to remove any undissolved polymer. The total solid content of the filtrate was then determined by gravimetric analysis.

The *freeze-pump-thaw* method was used to deoxygenate the polymer solution prior to the polymerisation. After deoxygenation, 0.01 M AIBN initiator was added under a nitrogen atmosphere, the solution immersed into an oil bath at 50°C, and samples were taken at fixed intervals for gravimetric analysis to monitor the conversion.

2.4. GPC procedure for molecular weight determination

Samples were dissolved in tetrahydrofuran (THF), filtered and injected, using a Waters WISP 710B automated injection system, into a series of four bed columns (B, C, C, D with size of 300 × 7.5 mm² — Polymer Labs) with detection by a differential refractive index detector (Waters 401). THF was used as eluent at a flow rate of 1 ml min⁻¹. The molecular weight distribution of *VneoD* was determined from calibration with a series of narrow poly(styrene) standards (Mark-Houwink constants: $K = 1.1 \times 10^{-5} \text{ dl g}^{-1}$, $\alpha = 0.725$), together with the Mark-Houwink constants for *VneoD* in THF [14]: $K = 7.26 \times 10^{-6} \text{ dl g}^{-1}$ and $\alpha = 0.716$.

2.5. GPC characterisation of the low molecular weight polyisoprene

The molecular weight distribution of the LMPI was characterised using GPC. Fig. 2 shows the GPC trace of the synthesised LMPI. A weight-average molecular weight of 2.8×10^4 was obtained, which is sufficiently low for homogeneous polymerisations.

2.6. NMR characterisation of the low molecular weight polyisoprene

NMR analysis was performed on a Bruker instrument at 300 MHz. The ¹H NMR spectrum of LMPI contains a mixture of 30% *cis* and 70% *trans*-1,4 repeating units. The assignments were determined from the literature [17]. The following peaks were identified in the ¹H NMR spectrum: δ (CDCl₃) 1.62 ppm, s, *trans* CH₃; 1.71 ppm, s, *cis* CH₃; 2.04–2.27 ppm, b, CH₂; 5.24 ppm, b, =CH-. Minor peaks from the initiator (*tert*-butyl hydroperoxide) were also observed at 0.97 and 1.31 ppm (from the CH₃ groups).

3. Modelling bulk conversion-time data

Simulations of the time evolution of conversion for the bulk free-radical polymerisation of *VneoD* (without any LMPI) were carried out as follows, using the diffusion-controlled model for termination of Russell et al. [18,19] Taking account of the chain-length dependence of the termination rate coefficient, the polymerisation rate at a given weight-fraction of polymer (instantaneous conversion) can be written as:

$$\frac{d[M]}{dt} = -k_p[M][R^*]; \quad \frac{d[R^*]}{dt} = 2fk_d[I] - 2\langle k_t \rangle [R^*]^2;$$

$$[I(t)] = [I(t=0)] e^{-k_d t} \quad (1)$$

where k_p and k_d are the rate coefficients for propagation and initiator dissociation, respectively, f the initiator efficiency, $[I]$ and $[M]$ the initiator and monomer concentrations, and $\langle k_t \rangle$ is the termination rate coefficient averaged over all degrees of polymerisation:

$$\langle k_t \rangle = \frac{\sum_{i,j} R_i R_j k_t^{ij}}{\left(\sum_i R_i\right)^2} \quad (2)$$

Here R_i is the concentration of radicals of degree of polymerisation i , and k_t^{ij} is the rate coefficient for termination between radicals of degree of polymerisation i and j . The R_i are found by solving the non-linear equations for this

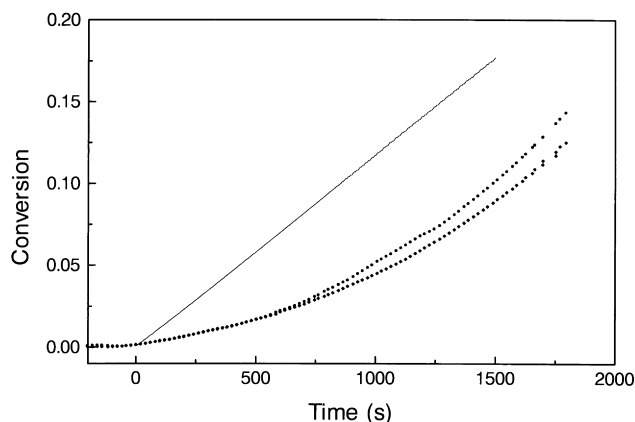


Fig. 3. Conversion as a function of time for polymerisations of bulk VneoD (50°C, 0.01 M AIBN). Unbroken lines: simulation; other curves: experiment.

quantity (in the steady state):

$$\frac{dR_i}{dt} = 0 = k_p(R_{i-1} - R_i)[M] - k_{tr,M}[M]R_i - 2R_i \sum_{j=1}^{\infty} k_t^{ij}R_j \quad (3)$$

where $k_{tr,M}$ is the rate coefficient for transfer to monomer. The chain-length-dependent rate coefficient k_t^{ij} is found (in a rubbery system such as the present one) using the diffusion model [18,19]:

$$k_t^{ij} = 2\pi p_{ij}(D_i + D_j)(r_i + r_j)N_A \quad (4)$$

Here D_i is the diffusion coefficient for diffusion of the radical end of an i -mer, $(r_i + r_j)$ is the radius of interaction for termination (taken here as the van der Waals radius), N_A is the Avogadro constant, and p_{ij} is the probability of reaction upon encounter (taken as 1/4 at low conversion). The diffusion coefficient at a given w_p is written as:

$$D_i(w_p) = \frac{D_{mon}(w_p)}{i^u(w_p)} \quad (5)$$

where D_{mon} is the diffusion coefficient of monomer and u is an exponent. Measurement of diffusion coefficients of a range of oligomers in a range of rubbery monomer/polymer matrices by pulsed-field gradient NMR [20] suggests that the following

Table 1

Literature values for the rate parameters for simulations of bulk polymerisation used in this work (the values of the remaining rate parameters are specified in the text)

Parameter	Literature value	Reference
k_p ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	5.2×10^3	[14]
k_d (s^{-1})	2.16×10^{-6}	[33]
f	0.7	[33]
$D_{mon}(w_p)$	Assumed same as for butyl methacrylate	[20]
$k_{tr,M}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	4	[34]
σ (nm)	0.6	[18]

Table 2

Concentrations of VneoD and LMPI used in bulk polymerisations

Run	[VneoD] (mol dm^{-3})	[LMPI] (mol dm^{-3})
1	3.74	2.11
2	4.22	0.71

empirical scaling “law” is obeyed over a range of conditions:

$$u(w_p)0.664 + 2.02 w_p \quad (6)$$

The w_p -dependence of D_{mon} for VneoD diffusing in a solution of polymer in its own monomer was taken to be the same as that for butyl methacrylate [20]. This approximation should not be a problem with regard to the question of seeing if the diffusion-controlled model can predict bulk polymerisation data, since the simulation results are not strongly sensitive to reasonable variations in this quantity, and moreover are sensitive to a number of other input parameters with similar uncertainties.

Given the various quantities set out in Eqs. (2)–(6), Eqs. (1) were then solved numerically.

4. Results and discussion

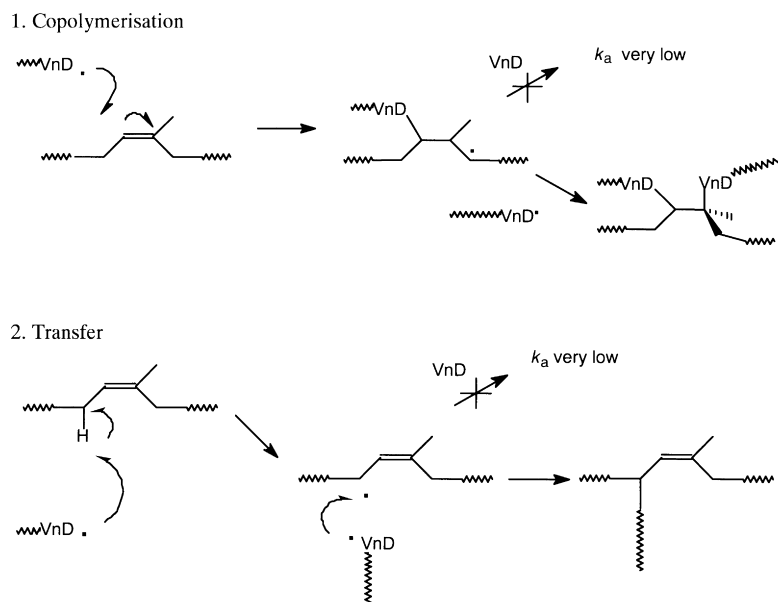
4.1. Bulk polymerisation

Bulk experiments of the polymerisation of VneoD were carried out at 50°C using AIBN as initiator. Fig. 3 shows that for pure bulk VneoD, the conversion reached approximately 15% in 30 min. The conversion-time data in the bulk experiments suggest retardation in the early stages of the reaction. After this retardation period, the observed rate is in accord with that simulated using the diffusion-controlled termination model developed by Russell et al. [18,19] with rate parameters from the literature (see Table 1). This suggests that the effects of retardation are not greatly significant for most of the bulk reaction. Such discrepancies as those observed in the conversion-time and rate data could be accounted for in terms of the uncertainties in several of the input parameters, including the rate coefficient for transfer to the monomer and the diffusion coefficient of the monomer at $w_p = 0$, to which the simulations are particularly sensitive.

4.2. Effect of LMPI

The addition of LMPI (Fig. 4) results in a dramatic retardation of the rate of reaction, well beyond the level of retardation observed early in the bulk situation (see Table 2 for concentrations of LMPI and VneoD used in these experiments).

As discussed in the Section 1, there are two free-radical mechanisms that could be used to explain such a dramatic effect (see Scheme 1, the two mechanisms used to describe the drastic retardation for VneoD in LMPI). The first is the copolymerisation (*addition*) mechanism: polymeric



Scheme 1.

VneOD radicals add across the backbone double bonds on polyisoprene to form radicals that are unreactive towards the monomer and now act as radical terminators, subsequently undergoing termination, grafting or crosslinking reactions. The second is the chain transfer mechanism (*abstraction* or *retardative chain transfer*), in which polymeric *VneOD* radicals abstract hydrogens from the allylic position on the polyisoprene backbone. Again these incipient radicals are supposed to be unreactive towards the monomer and to act as radical terminators.

A simple method to distinguish between these two mechanisms is the use of a model compound. Toluene was used in this work to test whether chain transfer was the more likely mechanism, since copolymerisation reactions with toluene are not possible. Fig. 5 shows conversion-time plots for the

polymerisations of *VneOD* in the presence of toluene (Table 3 lists the concentrations of toluene and *VneOD* used in these experiments). Retardation is seen, although not as drastic as that observed in the case of polyisoprene, and increases with the concentration of toluene.

The MWDs of *VneOD* polymerised in the presence of toluene at 50°C at conversions less than 10% are shown in Fig. 6. The entire molecular weight distribution shifts to lower weights with increasing toluene concentrations, as does the weight-average molecular weight (\bar{M}_w) (see Table 4). Further support for the hypothesis is that toluene fits the classical description as a retardative chain transfer agent [21]; it both reduces the rate and \bar{M}_w of *VneOD*. The results strongly support retardative chain transfer for the polymerisation of *VneOD* in the presence of polyisoprene,

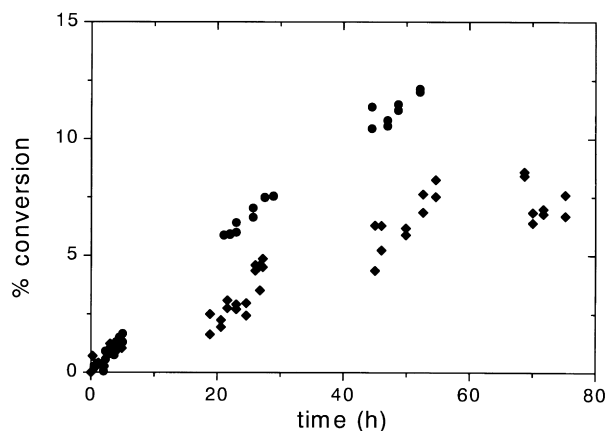


Fig. 4. Conversion versus time data for the polymerisation of *VneOD* in the presence of LMPI (50°C, 0.01 M AIBN, concentrations in Table 2), with the concentrations of LMPI being given in Table 4.

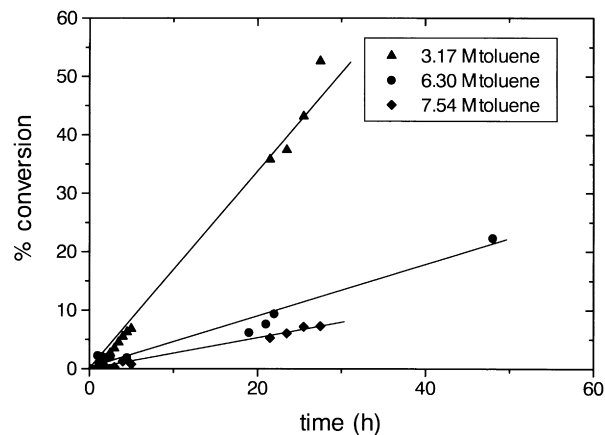


Fig. 5. Conversion versus time for polymerisation of *VneOD* at three different toluene concentrations (50°C, 0.01 M AIBN, toluene concentrations in Table 3).

Table 3
Concentrations of VneoD and toluene used for polymerisations to test chain or copolymerisation mechanisms

Run	[VneoD] (mol dm ⁻³)	[Toluene] (mol dm ⁻³)
3	2.95	3.17
4	1.48	6.30
5	0.88	7.54

a similar result to that found for VAc [6,7]. This implies that the polyisoprene radicals formed by the transfer reaction are very slow to react with VneoD. That is, the rate of propagation (reaction 2 in Scheme 2, kinetic description for retardative chain transfer in VneoD in the presence of toluene. The rate coefficients are as follows: $k_{tr,S}$ the rate coefficient for transfer to solvent (S), k_{tp} the rate coefficient for termination of the propagating radicals (P_n^*) with solvent radicals (S'), and $\langle k_t \rangle$ the average termination rate coefficient.) is far greater than that of re-initiation of the incipient radical formed by transfer (reaction 4). This also implies that the grafting reactions between the polyisoprene backbone and VneoD polymeric radicals readily occur to give short branches.

4.3. Determination of k_{tr} of VneoD to toluene from conversion-time data

The results can now be interpreted using the full kinetic description for retardative chain transfer. The kinetic scheme is shown in Scheme 2. The kinetic analysis of this scheme has been presented in detail elsewhere [15]. Approximate analytical solutions can be obtained by making the pseudo-steady-state approximation, a negligible rate of re-initiation (i.e. k_a is very low), a negligible rate of bimolecular termination, and time-independent initiator and

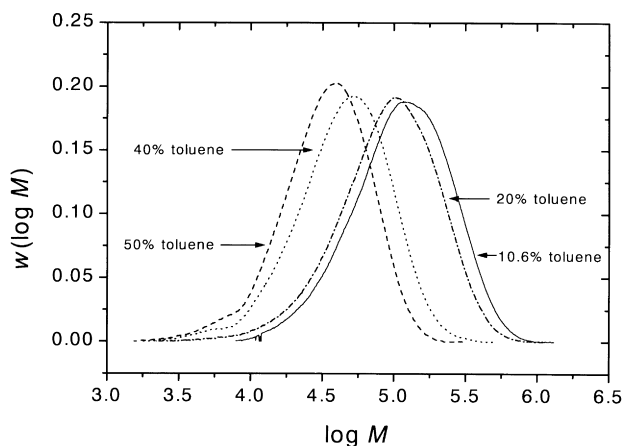


Fig. 6. The effect of increasing toluene concentration on the MWDs of poly(VneoD).

Table 4
The effect of toluene concentration on the \bar{M}_w of poly(VneoD)

Run	[VneoD] (mol dm ⁻³)	[Toluene] (mol dm ⁻³)	\bar{M}_w ($\times 10^{-4}$)
6	3.97	1.0	14.8
7	3.56	1.88	12.0
8	2.66	3.76	5.7
9	2.22	4.69	4.2

retarder concentrations. The equation thus obtained is:

$$\ln\left(\frac{[M]_0}{[M]}\right) = \frac{k_d k_p [I] t}{k_{tr,S} [S]} \quad (7)$$

where $[M]_0$ is the initial monomer concentration, $[S]$ the solvent (toluene) concentration (or the molar concentration of isoprene monomer units for reactions in the presence of polyisoprene), $k_{tr,S}$ the rate coefficient for transfer to solvent (or isoprene units) and t the reaction time. It has been previously shown by exact numerical solution of the complete rate equations [15] that the approximations leading to Eq. (7) are accurate.

Plots of $\ln([M]_0/[M])$ versus time, as suggested by Eq. (7), are shown in Fig. 5, and it can be seen that the expected linearity is obeyed to an acceptable approximation. The slope from each data set is then plotted versus $[toluene]^{-1}$ (Fig. 7), to calculate a value for $k_{tr,S}$ to toluene. The value thus obtained, using the parameters in Table 2, is $7.5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$.

4.4. Determination of k_{tr} of VneoD to toluene from molecular weight distributions

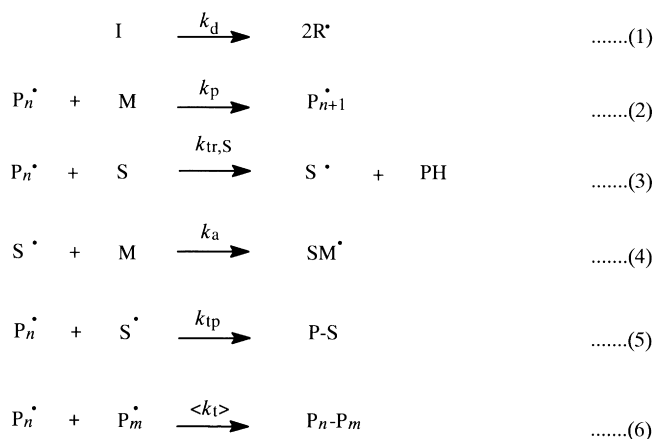
An alternative method to directly measure the k_{tr} to toluene is from the MWD via the $\ln P(M)$ method, described by Clay et al. [22] Here $P(M)$ is the number distribution of polymer chains with molecular weight M . The number distribution is obtained from the GPC distribution $w(\log M)$ using [22,23]

$$P(M) = \frac{w(\log M)}{M^2} \quad (8)$$

If conversion and the propagating free-radical concentration are both low, and making assumptions similar to those made above for the calculations from conversion-time data, one obtains [15]:

$$\lim_{M \rightarrow \infty, P_n \rightarrow 0} \ln P(M) = - \left\{ \frac{k_{tr,M} [M] + 2k_{tr,S} [S]}{k_p [M]} \right\} \frac{M}{M_0} \quad (9)$$

where P_n^* is the propagating radical concentration. It is implicit in Eq. (9) that $P(M)$ is the instantaneous number MWD (i.e. the number distribution of polymer formed at any instant), rather than the cumulative distribution as obtained by taking a sample from the reaction and measuring the MWD using GPC. In principle, the instantaneous distribution can be obtained by taking samples and closely



Scheme 2.

spaced conversions and subtracting the cumulative MWD at successive conversions [24]; in practice, this requires especially precise data. However, if data are obtained at low conversion, then the cumulative distribution is a good approximation to the instantaneous distribution.

The plots from the MWDs (Fig. 6) were converted to $\ln P(M)$ versus M as shown in Fig. 8a. There are extensive linear regions in which there are significant amounts of polymer (see Fig. 2). Following Eq. (9), the slopes of these linear regions are plotted against $[\text{VneoD}]/[\text{toluene}]$ in Fig. 8b, and from the gradient a value of $10.8 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for $k_{tr,S}$ to toluene is obtained. The values obtained by the two methods are given in Table 5. The transfer rate coefficients determined by both methods are in good agreement, which suggests that the conversion-time method is a valid alternative to obtain values for $k_{tr,S}$, given that the above assumptions are satisfied. In addition, the postulate that the free-radical chemistry of VneoD and VAc is very similar is strongly supported by the similarity of the k_{tr} values for VneoD and VAc to toluene (Table 5) and the similar retardation effect observed for both monomers in the presence of polyisoprene.

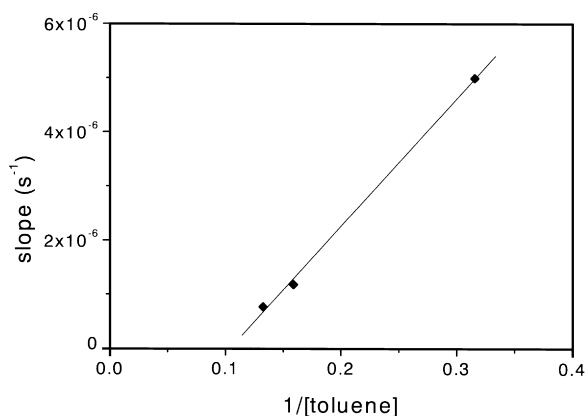


Fig. 7. Plots of the slopes from curves in Fig. 5 versus $[\text{toluene}]^{-1}$, used to determine the rate coefficient for transfer to toluene.

4.5. Determination of k_{tr} of VneoD to polyisoprene from conversion-time data

The subtraction method [22,24,25] for obtaining $\ln P(M)$ plots of the newly formed poly(VneoD), i.e. for finding the instantaneous molecular weight distribution, cannot be used in the polyisoprene system. This is because grafting reactions will invariably change the hydrodynamic volume of polyisoprene and consequently its elution volume (time) and apparent molecular weight distribution; therefore subtracting the GPC chromatogram of the pre-existing polyisoprene polymer from the blend in order to obtain an MWD of the newly formed poly(VneoD) would lead to gross errors. However, the conversion-time data can be used to obtain an approximate value of $k_{tr,P}$ for VneoD to polyisoprene.

Plots of $\ln([\text{VneoD}]_{t=0}/[\text{VneoD}]_t)$ versus time at 50°C are shown in Fig. 9a. The data can be treated in a similar manner to that of toluene, giving high correlation coefficients to the fits by linear regression. Plotting the slope from each data set versus $[\text{polyisoprene units}]^{-1}$ (Fig. 9b) allowed the $k_{tr,P}$ value of $150 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ to be obtained. This value is approximately an order of magnitude greater than that for toluene, and is similar to the value of $272 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ found at the same temperature for the corresponding transfer reaction of VneoD to polybutadiene [15]. It is thought that abstraction in toluene is mostly from the methyl hydrogens (i.e. primary carbon centre). It is postulated that the difference between k_{tr} to polyisoprene (or polybutadiene) and toluene is due first to the greater number of hydrogens available for abstraction on the polyisoprene unit in which more than half are attached to secondary carbon centres. Second, stabilisation of the incipient radicals through hyperconjugation [26] (where the radical stability is in the order of tertiary > secondary > primary > CH_4) has been shown to lower the activation energy for abstraction by methyl radicals from a primary to a secondary carbon by 7 kJ mol^{-1} in the gas phase, and has little or no effect on the frequency factor (A) for the rate coefficient [27]. This is in accord with

Table 5
Values for k_{tr} to toluene obtained from the conversion versus time data and $\ln(P(M))$

Monomer	Transfer agent (A)	$k_{tr,A}$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)	Method	Reference
VneoD	Toluene	7.5	Conv-time	This work
VneoD	Toluene	10.8	$\ln P(M)$	This work
VAc	Toluene	9.9	Mayo	[35]
VneoD	Polyisoprene	151	Conv-time	This work

the difference in activation energies of 6.7 kJ mol^{-1} between abstraction from toluene and polyisoprene calculated from this work at 50°C and assuming identical A values. Therefore, it is postulated that the majority of hydrogen abstraction by poly(VneoD) radicals is from the secondary carbon centres in polyisoprene. Although this postulate may seem reasonable, there is another postulate [15] that can also be used to explain such a difference in transfer rate coefficients between toluene and polyisoprene. The transfer reaction for poly(VneoD) radicals to polyisoprene could in

fact be under diffusion control [15], and therefore cannot simply be compared to the “chemically”-controlled reactions (i.e. reactions with a significant chemical barrier) of small benzyl radicals to polybutadiene. In addition, the type of diffusion control (i.e. “reaction” or “centre-of-mass” [18,19]) could substantially affect the Arrhenius parameters, depending upon the \bar{M}_w (in this case the \bar{M}_w of LMPI is approximately 3×10^4) and that of the attacking radical. The data presented here are insufficient to make any conclusions in this respect, as was also the case with analogous studies on polybutadiene [15].

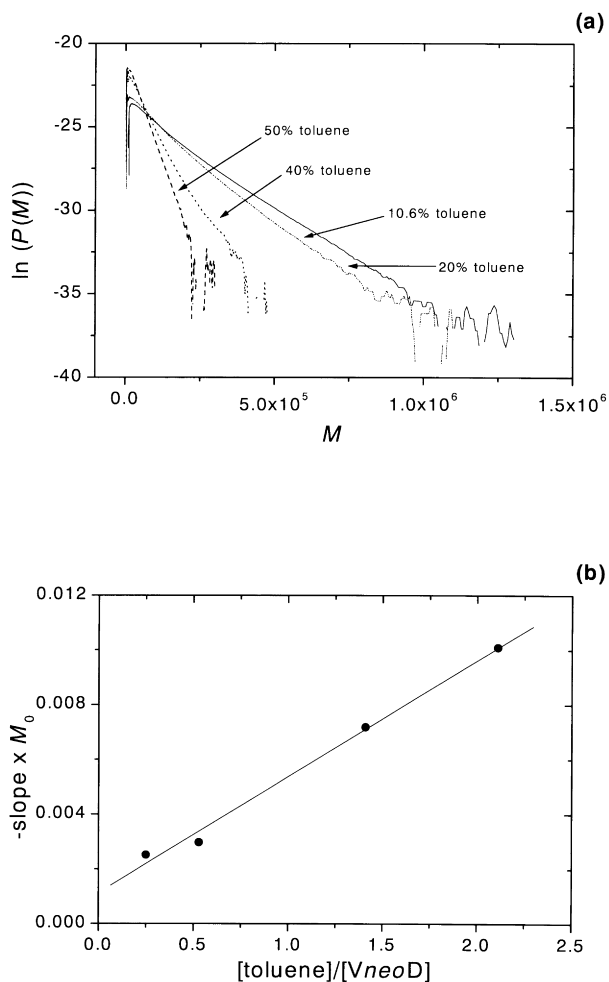


Fig. 8. (a) $\ln P(M)$ versus M of VneoD polymerised in the presence of toluene at 50°C for increasing toluene concentrations. Conversions were all below 10%; (b) plots of the slopes from curves in (a) versus $[\text{toluene}]/[\text{VneoD}]$, used to determine the rate coefficient for transfer to toluene (Eq. (9)).

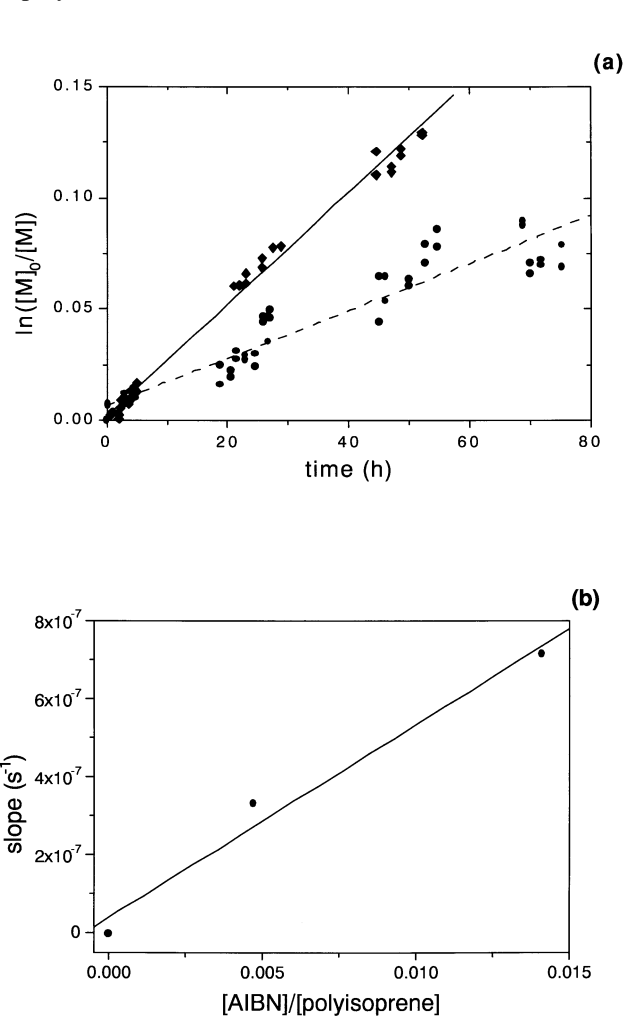


Fig. 9. (a) $\ln([M]_0/[M])$ versus time for polymerisations of VneoD carried out in the presence of increasing LMPI concentration at 50°C ; (b) plots of the slopes from curves (a) versus $[\text{LMPI}]^{-1}$ to determine the rate coefficient for transfer to LMPI (Eq. (7)).

In both cases the incipient radicals formed are further stabilised by resonance from the carbon–carbon double bonds and benzyl groups for polyisoprene and toluene, respectively. Stabilisation through resonance, in general, implies that the radicals are less reactive to further addition reactions [26,28]. This effect may be exacerbated by the type of monomer used in the system. For example, the experimental rate coefficients (k_a) for benzyl radical addition towards styrene and VAc at 50°C are 3.2×10^3 and $41 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, respectively [29], supporting the assumption that k_a is very low. However, the marked difference between these reactions cannot simply be ascribed to the difference of polarity in their transition states. Based on the e values from the Q-e scheme [30] (e values for STY and VAc are -0.8 and -0.88 , respectively), the nucleophilic benzyl radicals should be more reactive towards VAc. An alternative treatment is based on the so-called Revised Patterns Scheme [31], which predicts a value of $83 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for addition of the benzyl radical to VAc, based on the experimental value of $3.2 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ for styrene. A more complete explanation for such differences may involve an interplay between delocalisation, entropic, enthalpic and polar effects [29,32].

5. Conclusions

Bulk polymerisation of *VneoD* follows conventional kinetics and can be successfully modelled using conventional free-radical polymerisation with termination rate coefficients calculated from diffusion theory. However, bulk and solution polymerisations of *VneoD* in LMPI and toluene are strongly retarded. The data are consistent with the mechanism of retardative chain transfer. The abstraction of hydrogens from polyisoprene by polymeric *VneoD* radicals produces incipient radicals that are unreactive towards *VneoD* and act to terminate radicals to produce poly(*VneoD*) grafted to the polyisoprene backbone. It has also been shown that the conversion-time data can be used in the case of *VneoD*/toluene as an accurate alternative to the $\ln P(M)$ method to determine $k_{tr,s}$, and gives an approximate value of the rate coefficient for transfer to polyisoprene (although more data are needed to obtain an accurate transfer coefficient). The values obtained show that the rate coefficient for abstraction by poly(*VneoD*) radicals is an order of magnitude greater than that for toluene, which is postulated to be due to the greater number of secondary hydrogens available for abstraction and/or hyperconjugation effects. An alternative postulate is that this difference is because the reaction is under diffusion control when polymer–polymer reactions occur, and thus no conclusions may be drawn regarding this situation.

Acknowledgements

The authors gratefully acknowledge the support of the

Australian Research Council for both a Large and an Institutional Grant, and through the establishment and support of the Key Centre for Polymer Colloids. The authors are also glad to acknowledge the support of Atofina (BTTP) and of a Targeted Institutional Links grant from the Australian Department of Education, Training and Youth Affairs (NS).

References

- [1] Morton M. Science and technology of rubber. New York: Academic Press, 1978 (chap. 2).
- [2] Allen PW, Ayrey G, Moore CG, Scanlan J. *J Polym Sci* 1959;36:55.
- [3] Merrett FM. *Trans Faraday Soc* 1954;50:759.
- [4] Bloomfield GF, Swift PM. *J Appl Chem* 1955;5:605.
- [5] Allen PW. In: Bateman L, editor. Chemistry and physics of rubberlike substances. London: Maclaren, 1963 (p. 97).
- [6] Scanlan J. *Trans Farad Soc* 1954;50:756.
- [7] Allen PW, Merrett FM, Scanlan J. *Trans Faraday Soc* 1955;51:95.
- [8] Lehrle RS, Willis SL. *Polymer* 1997;38:5937.
- [9] Hawke BS. BSc (Hons) thesis, University of Sydney, 1974.
- [10] Gilbert RG. Emulsion polymerization: a mechanistic approach. London: Academic Press, 1995.
- [11] Ballard MJ, Napper DH, Gilbert RG. *J Polym Sci, Polym Chem Ed* 1984;22:3225.
- [12] Subramaniam N, Monteiro MJ, Taylor JR, Simpson-Gomes A, Gilbert RG. *Macromol Symp* 2000;152:43.
- [13] Subramaniam N, Balic R, Taylor JR, Griffiths M, Monteiro MJ, Gilbert RG, Ho CC, Abdullah I, Cacioli P. *J Nat Rubber Res* 1997;12:223.
- [14] Balic R, Gilbert RG, Zammit MD, Davis TP, Miller CM. *Macromolecules* 1997;30:3775.
- [15] Pham BTT, Tonge MP, Monteiro MJ, Gilbert RG. *Macromolecules* 2000;33:2383.
- [16] Anstey JF, Subramaniam N, Pham BTT, Lu X, Monteiro MJ, Gilbert RG. *Macromol Symp* 2000;150/151:73.
- [17] Tanaka Y, Takeuchi Y, Kobayashi M, Tadokoro H. *J Polym Sci, Part A-2* 1971;9:43.
- [18] Russell GT, Gilbert RG, Napper DH. *Macromolecules* 1992;25:2459.
- [19] Russell GT, Gilbert RG, Napper DH. *Macromolecules* 1993;26:3538.
- [20] Griffiths MC, Strauch J, Monteiro MJ, Gilbert RG. *Macromolecules* 1998;31:7835.
- [21] Odian G. Principles of polymerization. 3rd ed. New York: Wiley-Interscience, 1991.
- [22] Clay PA, Gilbert RG. *Macromolecules* 1995;28:552.
- [23] Short DW. *J Liq Chromatogr* 1993;16:3371.
- [24] Clay PA, Gilbert RG, Russell GT. *Macromolecules* 1997;30:1935.
- [25] Clay PA, Christie DI, Gilbert RG. In: Matyjaszewski K, editor. Advances in free-radical polymerization. ACS Symposium Series, vol. 685. Washington, DC: ACS, 1998 (p. 104).
- [26] Tedder JM. *Angew Chem, Int Ed Engl* 1982;21:401.
- [27] Gray PA, Herod AA, Jones A. *Chem Rev* 1971;71:257.
- [28] Giese B. *Angew Chem, Int Ed Engl* 1983;22:753.
- [29] Walbiner M, Qiang Wu J, Fischer H. *Helv Chim Acta* 1995;78:910.
- [30] Alfrey T, Price CC. *J Polym Sci* 1947;2:101.
- [31] Jenkins AD. *Polymer* 1999;40:7045.
- [32] Huang DM, Monteiro MJ, Gilbert RG. *Macromolecules* 1998;31:5175.
- [33] Moad G, Solomon DH. The chemistry of free radical polymerization. Oxford: Pergamon, 1995.
- [34] Balic R. PhD thesis. Sydney University, 2000.
- [35] Brandrup J, Immergut EH, Grulke EA. In: Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook, 4th ed. New York: Wiley, 1999.