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Free-Radical Kinetics of Grafting Reactions for Creating Novel Graft Copolymers in Emulsion Polymerization

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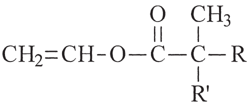
SUMMARY : The polymerization of vinyl neo-decanoate in the presence of polybutadiene has been studied. The rate of transfer to polymer has been determined, and has been found to be very high, resulting in the formation of a highly grafted copolymer.

Introduction

Chain transfer to polymer leads to branching and/or crosslinking in the final polymer, the extent of which can effect end-use properties. There are few reliable data in the literature for the rate coefficient of transfer to polymer and the site of transfer, a consequence of the difficulties involved experimentally. Recently, Lovell *et al.* gave evidence that chain transfer to polymer in free-radical homopolymerizations and copolymerization of *n*-butyl acrylate involves abstraction of hydrogen atoms from backbone tertiary C-H bonds,[1-4] whilst chain transfer to polymer in the free-radical homopolymerization of vinyl acetate takes place via hydrogen abstraction from the methylene group[5]. Such chain transfer is expected to be especially strong in vinyl alkanoates (e.g. vinyl acetate).

A monomer which is expected to have very similar chemistry to vinyl acetate is vinyl neo-decanoate (VneoD):



$$CH_2{=}CH{-}O{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\underset{\underset{\displaystyle R'}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}{-}R$$

(the commercial monomer is a mixture of isomers, where the total number of carbons in R and R' is 7). For example, the Arrhenius parameters for propagation of these two monomers are very similar.[6] Recent work in this laboratory with solution and emulsion polymerization of VneoD in the presence of polyisoprene[7-8] showed a large amount of retardation and evidence of extensive grafting. The data were qualitatively consistent with a mechanism of

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retardative chain transfer. In this mechanism, short polyVneoD chains are grafted onto the backbone of polyisoprene. Huang and Sundberg[9-12)] proposed that the high reactivity of the acrylate is due to both abstraction from the allylic hydrogen and addition across the double bonds in polybutadiene. Based on this grafting mechanism, the resultant copolymer would consist of a low number of grafted chains, which have long chain lengths.

The purpose of this paper is a kinetic study of the mechanism of grafting reactions in the polymerization of vinyl neo-decanoate in the presence of polybutadiene. The study attempts to determine (a) whether retardative chain transfer is a mechanism at play for the VneoD/polybutadiene system and (b) the rate coefficient for transfer of a hydrogen atom from the polybutadiene backbone by VneoD radicals. The Arrhenius parameters will then be examined in an attempt to determine the mechanism of the reaction process, which is between two polymer chains (a VneoD macroradical and polybutadiene): specifically, to see if it is controlled by the diffusion of the radical chain end, or by the “chemical” step of the actual abstraction.

Experimental

The bulk polymerization of VneoD is carried out by dilatometry at 50, 70 and 90°C in the presence of various amounts of low molecular weight polybutadiene, using AIBN as initiator. All polymerizations were carried out to conversions below 20% to avoid inefficient mixing due to the formation of a gel. Absolute molecular weights of the polymer were obtained from the molecular weights relative to polystyrene using the Mark-Houwink-Sakaruda parameters $K = 1.1\text{x}10^{-5}$ dL g^{-1}, $\alpha = 0.725$ for polystyrene,[13)] and $K = 7.26\text{x}10^{-5}$ dL g^{-1}, $\alpha = 0.716$ for pVneoD.[6)] The results for the molecular weight distribution so obtained, which assumes an unbranched chain of pure VneoD, are only be semi-quantitative, since the actual polymer may be a polybutadiene/VneoD graft copolymer.

Results and Discussion

The data for a range of monomer, polybutadiene and initiator concentrations at 50–90°C in Fig. 1 show that the polymerization rate is decreased when small amounts of polybutadiene are present. This is qualitatively consistent with the retardative chain transfer mechanism suggested for polyisoprene. In order to further characterize this as the mechanism at play, the data were compared with the behavior predicted from the kinetic scheme for retardative chain transfer. It is also important to note that all data exhibit an inhibition period, probably due to presence of oxygen. This period was taken into account for simulations and kinetic parameter determination.

Kinetic analysis

The retardative chain transfer mechanism postulated here is as follows:

$$I \xrightarrow{k_d} 2R^\bullet \tag{1}$$

$$M_n^\bullet + M \xrightarrow{k_p} M_{n+1}^\bullet \tag{2}$$

$$M_n^\bullet + S \xrightarrow{k_{tr,P}} S^\bullet + M_nH \tag{3}$$

$$S^\bullet + M \xrightarrow{k_a} SM^\bullet \tag{4}$$

$$M_n^\bullet + S^\bullet \xrightarrow{<k_{tp}>} SM \tag{5}$$

$$M_n^\bullet + M_n^\bullet \xrightarrow{<k_t>} M_n - M_n \tag{6}$$

where I = initiator, M = VneoD, S = butadiene monomer unit in polybutadiene, $R^\bullet$ = initiator-derived radical. The species resulting from the transfer of a hydrogen from butadiene to a polyVneoD radical is presumably an allylic polybutadiene radical.

The rate equations corresponding to these reactions are solved numerically, as discussed later. Kinetic analysis is facilitated through approximate analytic solutions obtained by assuming a time-independent [I] [eq (1)], negligible re-initiation (k_a = 0) and ignoring the homotermination reaction (k_t =0). One then obtains

$$\ln\frac{[M_o]}{[M]} = \frac{f\,k_d k_p}{k_{tr,P}}\frac{[I]}{[S]}t \tag{7}$$

Under these assumptions, a plot of $\ln[M_0]/[M]$ vs. time should be linear. Indeed this behavior is seen experimentally to an acceptable approximation, as shown in Figures 1, making due allowance for the existence of a variable induction period. The experimental slope S_{exp} of such a plot (i.e., of the linear region of $\ln[M_0]/[M]$) should yield $fk_dk_p/k_{tr,P}$. Hence plots of S_{exp} against [I]/[S] for a series of runs with different [I] and [S] should also be linear. Again this is in acceptable accord with experiment, as seen in Fig. 2.

GPC Analysis of PolyVnD

If the reaction follows the kinetics mentioned above and the assumptions leading to eq 7 are valid, the number-average molecular weight $<M_n>$ is given by:[14)]

$$< M_{n'} >= \frac{k_p[M]}{k_{tr,P}[S]} M_o \tag{8}$$

where M_0 is the molecular weight of VneoD monomer. The values of $<M_n>$ predicted by eq 8 and those observed experimentally, which are closed together do not contradict the quantitative mechanistic interpretation, and qualitatively supports the main chain-stopping event is transfer from polybutadiene by polyVneoD radicals.

Arrhenius parameters

The values obtained for S_{exp} for each temperature are shown in an Arrhenius form in Fig. 3; the data fit $\ln S_{exp}/\mathrm{s}^{-1} = 10^{17.6} \exp(-138\ \mathrm{kJ\ mol}^{-1}RT)$. These values of S_{exp} can be used to obtain values of $k_{tr,P}$ at each temperature, given values of f, k_d and k_p. Unfortunately, this data reduction to obtain $k_{tr,P}$ is subject to high uncertainty, since the values of $k_{tr,P}$ are very sensitive to uncertainties in the activation energies of k_d and k_p, especially because of the high activation energy for k_d, and the relatively large uncertainties in the values of S_{exp}. Because of this high uncertainty, an error analysis of the resulting values of $k_{tr,P}$ is essential. This was done in an admittedly simplistic way by assuming an uncertainty of ±2 and ±1 kJ mol^{-1} in k_d and k_p respectively, using these uncertainties together with those in the values of S_{exp} to find the maximum and minimum possible values of $k_{tr,P}$, and taking these together with the mean values of this last quantity to generate χ^2 for a non-linear fit of the Arrhenius equation to these collected values of $k_{tr,P}$. The minimum in χ^2 so obtained is $\mathrm{k}_{tr,P}$ / $\mathrm{dm}^3\ \mathrm{mol}^{-1}\ \mathrm{s}^{-1} = 10^{6.1} \exp(-25.7\ \mathrm{kJ\ mol}^{-1}/\mathrm{RT})$, with the 95% contour for χ^2.

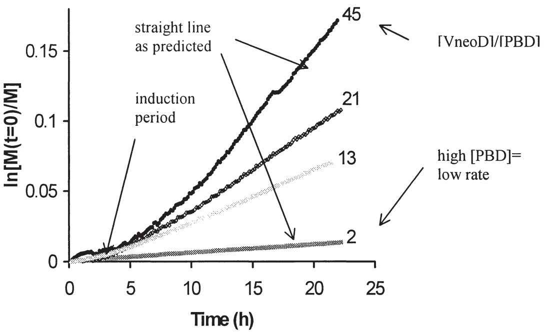

Fig 1: Plot of $\ln([M_o]/[M])$ vs time obtained at 50°C

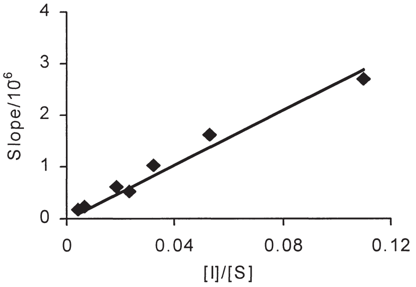

Fig 2: Dependence of slopes S_{exp} on the ratio of initiator to polybutadiene concentration at 50°C

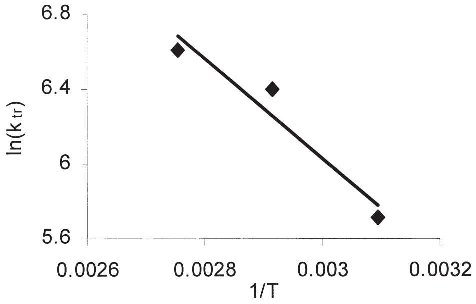

Fig 3: Arrhenius plot of rate coefficient for chain transfer to polymer $k_{tr,P}$

Conclusions

The retardative chain transfer mechanism is valid for vinyl neo-decanoate (VneoD) polymerization in polybutadiene, resulting in a highly grafted polymer microstructure. The rate coefficient for transfer to polymer were found to be $k_{tr,P}$ / dm^3 mol^{-1} s^{-1} = $10^{6.1}$ exp(–25.7 kJ mol^{-1}/RT), subject to high uncertainties. The results are consistent with the process being controlled either by the transfer step having a surprisingly low activation energy, or by the diffusion of the radical chain end, both by center-of-mass diffusion and "reaction-diffusion".

Acknowledgments

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