

Anionic Copolymerization of Butadiene and Isoprene: Applicability of the Terminal Model to High Conversion

D.J.T. Hill¹, J.H. O'Donnell^{1*}, P.W. O'Sullivan¹, J.E. McGrath², I.C. Wang² and T.C. Ward²

¹ Polymer and Radiation Group, Department of Chemistry, University of Queensland, Brisbane 4067, Australia

² Department of Chemistry, Polymer Materials and Interfaces Laboratory, Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

SUMMARY

The compositions of copolymers of butadiene (B) and isoprene (I), produced by anionic copolymerization with *sec*-butyl lithium initiator in hexane at 20-40°C gave a good fit at low conversions to the terminal model for copolymerization. Non-linear, "best estimates" of the reactivity ratios r_B and r_I were 2.82 and 0.42, 1.72 and 0.36, 2.18 and 0.35 at 20, 30 and 40°C. The rates of copolymerization at conversions up to 98% of total monomer gave a smooth relationship with the instantaneous feed composition, calculated using the terminal model, at each temperature and independent of the initial feed composition. These results are in accord with the terminal model being applicable to this anionic copolymerization from low to high conversions.

INTRODUCTION

The homogenous homopolymerizations of butadiene, isoprene and styrene without termination can be studied using alkyl lithium initiators in non-polar solvents, such as hexane, cyclohexane or benzene (NOSHAY and McGRATH, 1977). The relative rates of homopolymerization are styrene > isoprene > butadiene.

Copolymerizations of the monomer pairs, styrene-butadiene (KOROTKOV and CHESNOKOVA, 1960) and styrene-isoprene (KOROTKOV and RAKOVA, 1961) have been studied under these conditions. The copolymer formed initially was predominantly diene. Only when the diene was depleted did the styrene content of the copolymer increase.

* To whom correspondence should be addressed

The rate of copolymerization showed a sudden increase to that of styrene homopolymerization at the conversion corresponding to consumption of the diene in the feed. The predominance in the initial stage of the copolymerization of the monomer which has the lower rate of homopolymerization has been referred to as a "reversal" or "inversion" of reactivity.

RAKOVA and KOROTKOV(1958) have reported that the initial rates of copolymerization of isoprene and butadiene corresponded to the homopolymerization of butadiene, which is the less reactive monomer. WANG *et al.* (1981) have recently studied the copolymer compositions at low conversion and the copolymerization rates to very high conversion, using sec-butyl lithium initiator. The copolymerization rate curves varied smoothly with initial feed composition from pure butadiene to pure isoprene, in contrast to the results reported for styrene-isoprene and styrene-butadiene.

Since the sharp discontinuities in the rates of copolymerization observed in these systems were not found for isoprene-butadiene, we have examined whether the copolymerization rates to high conversions are compatible with the reactivity ratios obtained by applying the terminal model of copolymerization to the copolymer compositions at low conversions.

EXPERIMENTAL

Butadiene and isoprene monomers, hexane solvent and sec-butyl lithium initiator were purified according to previously described methods (MORTON and FETTERS, 1975). The monomer/solvent/initiator mixtures were prepared under high vacuum, with flaming of the apparatus. Rates of polymerization were measured in glass dilatometers and checked by precipitation of the copolymers with methanol, drying in vacuum at 25°C and weighing (WANG *et al.*, 1981). Polymer compositions were determined by ^1H NMR.

RESULTS AND DISCUSSION

Reactivity Ratios

The non-linear least squares computational procedures which we have described previously (CAIS *et al.*, 1979) have been applied to the comonomer/copolymer composition data (WANG *et al.*, 1981) at low conversions to give "best estimates" of the reactivity ratios for the terminal model of copolymerization, with

Table 1: Calculated reactivity ratios for the anionic copolymerization of butadiene (B) with isoprene (I)

T/°C		Reactivity Ratios	
		(a)	(b)
20	r_B	2.62	2.82
	r_I	0.40	0.42
	S^e	1.72×10^{-4}	1.28×10^{-4}
30	r_B	1.60	1.72
	r_I	0.35	0.36
	S	1.10×10^{-4}	1.00×10^{-5}
40	r_B	1.89	2.18
	r_I	0.32	0.35
	S	1.53×10^{-3}	2.75×10^{-4}

- a) Kelen-Tudos method
 b) Non-linear least squares method (with account of conversion)
 c) S = Sum of squares of differences between calculated and experimental compositions divided by $n-p$, where n = number of experimental points, and p = number of variable parameters.
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allowances for the experimental conversions. These reactivity ratios and the standard errors of the polymer compositions (goodness-of-fit parameters) are compared with the values obtained using the Kelen-Tudos method in Table 1. The estimates of the reactivity ratios show small differences, and the standard errors in the polymer compositions a moderate improvement, using the non-linear fit of experimental data.

Instantaneous Feed Compositions

The reactivity ratios shown in Table 1 can be used to calculate the instantaneous monomer feed compositions as a function of conversion for any initial feed composition. The comonomer composition/conversion relationships at 40°C for initial isoprene mole fractions of 0.25, 0.5 and 0.75 are shown in Fig.1. Similar relationships are obtained at 20 and 30°C.

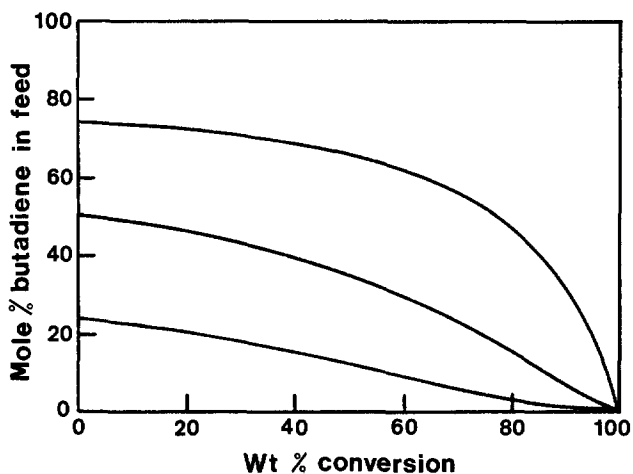


Fig.1 - Instantaneous monomer feed compositions at 40°C for initial compositions of 25, 50 and 75 mole % butadiene as functions of conversion calculated for the terminal model of copolymerization using the reactivity ratios in Table 1 case (b).

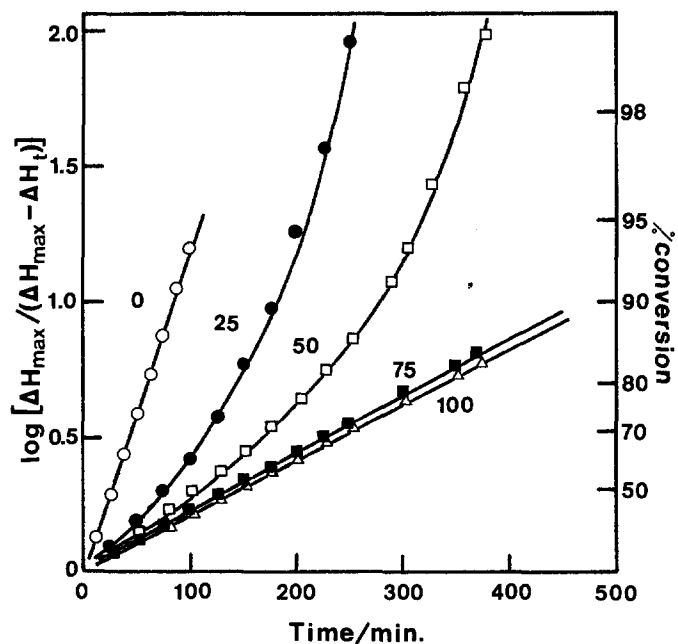


Fig.2 - Dilatometric measurements of the rates of copolymerization at 40°C for different initial feed compositions (mole % butadiene).

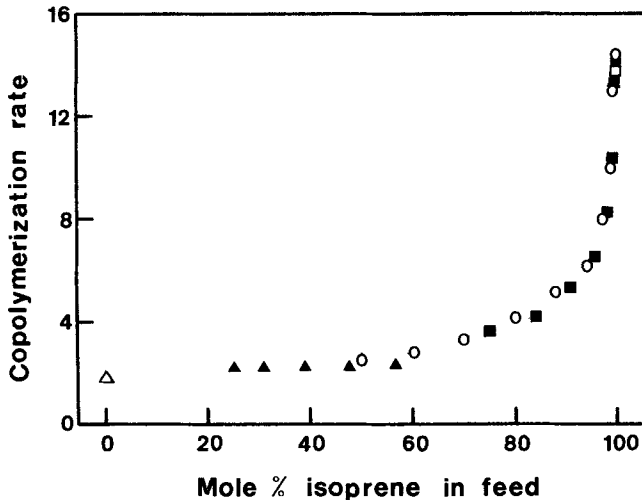


Fig.3 - The dependence of the instantaneous rate of copolymerization at 40°C on the instantaneous monomer feed composition, calculated using the information in Figs. 1 and 2. Initial monomer feed compositions: (Δ) 0%; (▲) 25%; (○) 50%; (■) 75%; (◻) 100% isoprene.

Kinetics to High Conversion

The dilatometric kinetic curves (WANG *et al.*, 1981) at 40°C are shown in Fig.2. The quantity plotted on the ordinate is a logarithmic function of conversion (ΔH_{\max} and ΔH_t are dilatometric heights at complete conversion (max) and at time t), from which the conversions can be derived.

The instantaneous copolymerization rates can be calculated by taking the slopes of the kinetic plots in Fig.2. Utilizing the calculated compositions in Fig.1, it is possible to obtain the relationship between instantaneous copolymerization rate and comonomer feed composition throughout each kinetic run, i.e. from low to high (98%) conversion.

The results of these calculations are shown in Fig.3. It is apparent that (i) a continuous curve is obtained from pure butadiene to pure isoprene, and (ii)

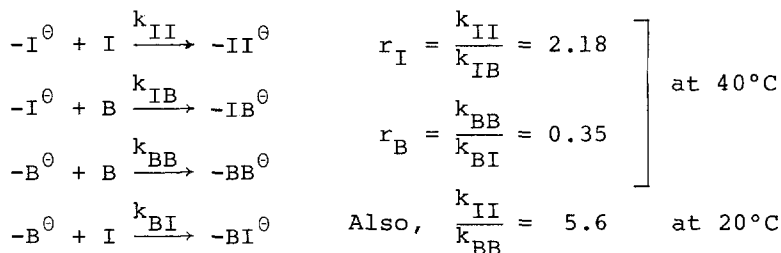
the values at high conversion for one initial feed composition are identical with those at low conversion for a different initial feed composition.

These two features of Fig.3 indicate that the copolymerization can be described, at least to a first-order approximation, by the same parameters from low to high conversions, i.e. by the two reactivity ratios of the terminal model.

The relationship shown in Fig.3 is similar to that observed for most free radical copolymerizations. The deviation from linearity with feed composition is then attributed to enhanced cross-termination compared with homo-termination. However, the copolymerization of butadiene and isoprene is a "living" anionic reaction without termination. Therefore, the variation in rate shown in Fig.3 must be due to the propagation reactions. The butadiene plays a dominant kinetic role as a retardant through the cross propagation reaction $-I^\ominus + B \rightarrow -IB^\ominus$. This has been attributed to the difference in strength of the propagating anion - lithium counterion interaction for butadiene and isoprene. The propagation mechanism is summarized in Table 2.

The reactivity ratio r_B shows a minimum at 30°C, as does the product $r_B r_I$, which is unexplained. However, the reactivity ratios deduced by previous workers (RAKOVA and KOROTKOV, 1959) at 50°C are compatible with the values derived from WANG *et al.* (1981) at 30 and 40°C.

Table 2 Propagation reactions, reactivity ratios and rate constants for the terminal model.



ACKNOWLEDGEMENTS

The authors wish to thank the Australian Research Grants Scheme and the US Army Research Office for supporting this work.

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Accepted December 21, 1982