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## Initiation phenomena in the emulsion polymerization of butadiene and isoprene

P. A. Weerts, J. L. M. van der Loos and A. L. German\*

Laboratory of Polymer Chemistry, Eindhoven University of Technology, PO Box 513, 5600 MB Eindhoven, The Netherlands

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The emulsion polymerizations of butadiene and isoprene are highly insensitive to the nature and concentration of the investigated initiators. This is a result of the low initiator efficiency with regard to particle formation. Furthermore, the promoting effect of mercaptans is specific of the persulphate-initiated polymerizations. The formation of sulphate-initiated oligomeric radicals is likely to be severely retarded.

(Keywords: emulsion polymerization; butadiene; isoprene; initiation; promoting effect; mercaptan)

### INTRODUCTION

In earlier investigations of emulsion polymerization it was found that the rate of (co)polymerization of butadiene(75)–styrene(25) or butadiene alone was unaffected when the concentration of persulphate was changed within wide limits<sup>1</sup>. Furthermore, small amounts of mercaptans seemed to be essential to bring about reaction at acceptable rates<sup>2</sup>. This unexplained effect is referred to as the promoting effect of mercaptans. In contrast to these findings, other authors<sup>3,4</sup> did not observe any promoting effect of dialkyl xanthogen disulphides in butadiene polymerizations with 4,4'-azo-bis-4-cyanopentanoic acid as the initiator, but even a slight retardation. Since these (co)monomer systems are of great industrial importance, it was felt necessary to look more closely into these unusual features. With this aim, a study was undertaken of the emulsion polymerization of butadiene and isoprene with different initiator systems. The initiators used were water-soluble potassium persulphate (PPS), amphiphilic 4,4'-azo-bis-4-cyanopentanoic acid (ACPA) and oil-soluble 2,2'-azo-bis-isobutyronitrile (AIBN). The effects of these initiators were studied in the presence and absence of tertiary dodecyl mercaptan (TDM).

### EXPERIMENTAL

The *ab initio* polymerizations were carried out in stainless steel reactors (1 and 3 litre reaction volumes). Conversion data were based on total solids determinations. The diameters of the latex particles were measured with dynamic light scattering (Malvern IIc) and occasionally verified with electron microscopy. The particle number at different conversions was calculated from the measured diameter, polymer content and polymerization recipe (Table 1).

### RESULTS AND DISCUSSION

The experimental results with varying initiator concentrations in the presence of TDM are given in Table 2. It is evident that the overall kinetics of these

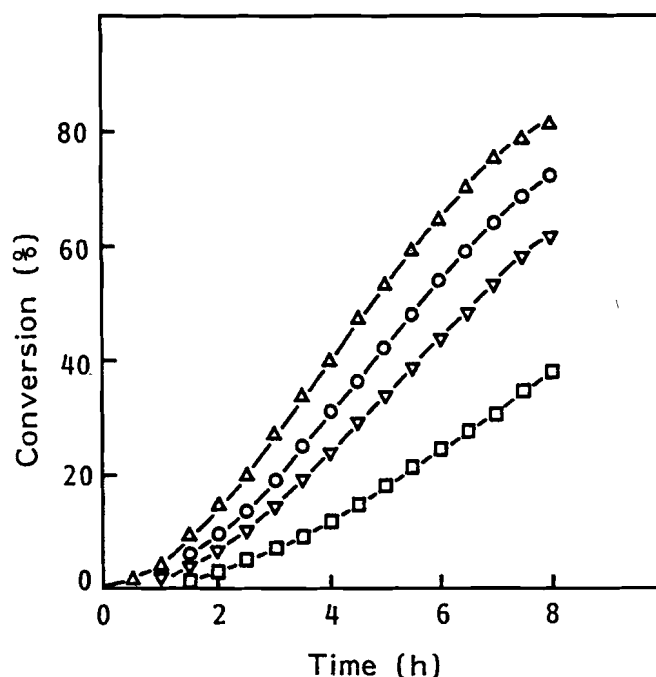


Figure 1 Conversion–time curves of persulphate-initiated polymerizations at different initiator concentrations:  $\Delta$ , 13.2;  $\circ$ , 2.6;  $\nabla$ , 0.53;  $\square$ , 0.27 mmol kg<sup>-1</sup> water

Table 1 Polymerization recipe in parts by weight

Water	230
Monomer	100
Dresinate 214	7.6
Potassium carbonate	4.4
Initiator	variable
(mixed) TDM	0.0 or 0.7
Temperature	62°C with butadiene 67°C with isoprene
pH	10.5–10.8

polymerizations are hardly affected by the nature and concentration of the initiators in the concentration ranges studied. Table 3 shows that in the ACPA- and AIBN-initiated polymerizations TDM causes no significant retardation. On the other hand, Table 3 also clearly

\* To whom correspondence should be addressed

**Table 2** Polymerizations of dienes in the presence of TDM

Polymerization system	[I] (mmol kg <sup>-1</sup> water)	R <sub>p</sub> (% h <sup>-1</sup> )	d <sub>90</sub> (nm)	N × 10 <sup>-14</sup> (g <sup>-1</sup> water)	R <sub>p</sub> /N × 10 <sup>20</sup> (g polymer s <sup>-1</sup> )
Bu-PPS	13.2	12.6	107	6.2	2.4
	13.2	12.0	112	5.7	2.5
	6.6	12.2	109	6.3	2.3
	2.6	11.3	109	6.4	2.1
	0.53	9.7	113	5.8	2.0
	0.27	8.7	122	4.7	2.2
Bu-ACPA	13.2	12.4	110	6.0	2.5
	13.2	13.2	109	6.2	2.5
	4.4	11.4	114	5.5	2.5
	0.66	9.6	119	4.8	2.4
Bu-AIBN	26.4	13.2	110	6.4	2.5
	13.2	12.6	107	6.1	2.5
	4.4	12.6	108	6.8	2.2
Iso-PPS	13.2	15.0	116	5.2	3.4
	13.2	15.1	116	5.3	3.5
	6.6	14.4	115	5.7	3.1
	1.3	14.0	117	5.0	3.4

R<sub>p</sub>=constant rate of polymerization in interval II, d<sub>90</sub>=average particle diameter at 90% conversion, N=average number of particles at high conversions, Bu=butadiene, Iso=isoprene, I=initiator

**Table 3** Effect of TDM on diene polymerizations with different initiators

Polymerization system	% conversion after				R <sub>p</sub> (% h <sup>-1</sup> )	d <sub>90</sub> (nm)
	4 h	6 h	8 h	24 h		
Bu: PPS/TDM	39	63	80	99	12.6	107
PPS	6	7	7	10	—	—
ACPA/TDM	38	67	84	100	13.2	109
ACPA	39	65	82	100	13.3	107
AIBN/TDM	37	62	80	99	12.6	107
AIBN	40	63	79	100	12.9	111
Iso: PPS/TDM	56	76	86	96	15.1	116
PPS	5	7	8	12	—	—
ACPA	56	77	88	100	15.8	111
AIBN	59	78	88	99	16.1	106

[I]=13 mmol l<sup>-1</sup>, temperature=62°C for butadiene and 67°C for isoprene

reveals that the promoting effect of TDM is typical of the persulphate-initiated polymerizations.

Inspection of the conversion-time curves (Figure 1) indicates that particle formation is a slow process since interval I is unusually long, 2 h or more. The total number of primary radicals generated during this period is 10<sup>17</sup>–10<sup>18</sup> g<sup>-1</sup> water. The final particle number is about 5 × 10<sup>14</sup> g<sup>-1</sup> water. This large difference implies that all three initiators investigated are very inefficient in the particle formation process. Therefore, the variation of initiator concentration in the studied regions will hardly affect polymerization kinetics. In the case of water-soluble initiators, transfer of radical activity from the aqueous phase into a micelle or latex particle is facilitated by surface active oligomeric radicals which will be adsorbed on the surface. In order to compete successfully with the emulsifier for adsorption the oligomeric radicals have to be sufficiently lipophilic. If these oligomers undergo aqueous phase termination before they have grown into mature surface-active species then the polymerization will be severely retarded. Such a situation might occur in the case of the diene/PPS system when no mercaptan is available. In the presence of mercaptan an alternative mechanism is operative. As postulated earlier<sup>5</sup>, the mercaptan forms a redox system with the persulphate which generates mercaptanyl radicals. The lipophilic and neutral radicals may easily enter a micelle or particle and

initiate polymerization. The question remains why the promoting effect is restricted to the diene/PPS system. After all, it is a well-known fact that mercaptans hardly influence the polymerization of styrene, a monomer of comparably low water solubility. We believe that the slow diene/PPS polymerization without mercaptan is caused by a relatively fast aqueous phase termination mainly due to two factors. First, the diene monomers have a significantly lower reactivity than styrene. Second, the growing oligomeric radicals have to reach a critical hydrophilic-lipophilic balance (HLB), which requires more diene molecules than styrene molecules to be added to a primary radical. These factors would retard the process of oligomer formation and aqueous phase termination may become predominant, leading to very slow diene polymerizations. The role of the initiator is even more obscure. The results indicate that the water solubility and charge of the initiating radicals are irrelevant parameters. Under the experimental conditions ACPA will be deprotonated and thus the primary radicals will be charged and rather water-soluble. The key to fully understanding the promoting effect might well lie in a delicate balance between the reactivities of the monomer and the initiating radical fragments. Research is continuing in studying the effects of other relevant reaction parameters, such as the emulsifier concentration, the monomer-water ratio and the amount of mercaptan. Results will be reported in separate publications.

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