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Use of Cryptates in Bulk Anionic Polymerization of Dienes

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ABSTRACT

The bulk polymerization of isoprene and butadiene with organoalkali compounds in the presence of cryptants has been studied. The effects of monomer concentration, cryptant concentration, and counterions on the induction period and molecular weight with these same monomers has also been studied. The microstructure of polymers has been determined by ¹H-NMR measurements. In the presence of complexed ion pairs the structure is independent of the temperature, of the initiator concentration, of the counterions, and of the organoalkali/cryptant molar ratio, but the vinyl structure increases with the cryptant concentration.

INTRODUCTION

It is established that polymerization and oligomerization of diene monomers constitute an important part of the polymerization field. The properties of diene depend on the way in which the monomer is incorporated into the chain with the possibility of polymerization following several pathways: 1-4, 1-2, and possibly 3-4 additions. This configuration of the polymer essentially depends upon the nature of reactions performed [1-8]. Thus it is not surprising that chemists have tried to devise conditions allowing definite mixtures of the possible products or of one of them to be obtained.

In particular, anionic polymerization led to variation of the relative proportions of the possible additions. The organoalkali which initiated polymerization of diene has been the subject of intensive study in the last years [1-13], and it is well known that variation of the counterion and of the solvent leads to variations of configuration. For example, polymerization of butadiene or isoprene by lithium or organolithium reagents in hydrocarbon solvents essentially lead to 1-4 products [1, 2]. On the other hand, 1-2 and 3-4 products were mainly formed in polar media [3].

High resolution NMR studies have been carried out in order to obtain information on the polymerization mechanism by studying the propagating living species. Several published investigations of the propagation reactions have mostly acknowledged the difficulty of ascertaining whether the slow initiation reaction has gone to completion. The effect of additives, particularly ethers and amines on the kinetics of polymerization and microstructures of the polymers produced, has been studied in detail [8]. However, no bulk polymerization of these monomers by cryptant addition on organoalkali compounds has yet been published.

In the present paper we report the results obtained in this field. A more detailed study of the influence of the polymerization parameters is also reported.

EXPERIMENTAL

Materials and Polymerization Procedure

Reagent grade butadiene (95.9% was used without further purification).

Isoprene (Aldrich Chemical Co.) was distilled on calcium hydride.

The purification of cryptants and the experimental technique used in this study were outlined in a preceding paper [4].

Alkali naphthalene was prepared by reaction of the naphthalene on a metallic mirror in THF in the presence of cryptant at room temperature. For bulk polymerization the solvent was removed by vacuum distillation beforehand.

Analytical Data

Molecular weight measurements were obtained by VPO with a Knauer instrument.

Polybutadiene and polyisoprene structures were determined by $^1\text{H-NMR}$ measurements. $^1\text{H-NMR}$ spectra were measured in 10-20% polymer solution in carbon tetrachloride with a Perkin-Elmer spectrometer (R12).

The structure assignments were made using the Tanaka method [15] for polybutadiene and the Pham method [16] for polyisoprene.

RESULTS AND DISCUSSION

All reaction plots which were obtained, whether or not in the presence of cryptants, were of the form shown in Fig. 1.

Initially the rate of polymerization was low; it then increased very rapidly. This behavior is similar to that observed for cryptates-initiated bulk polymerization of methyl methacrylate [14]. Induction periods were found to be a genuine feature of these polymerizations and were relatively reproducible. Contrary to MMA, long induction periods of several minutes duration were normally observed.

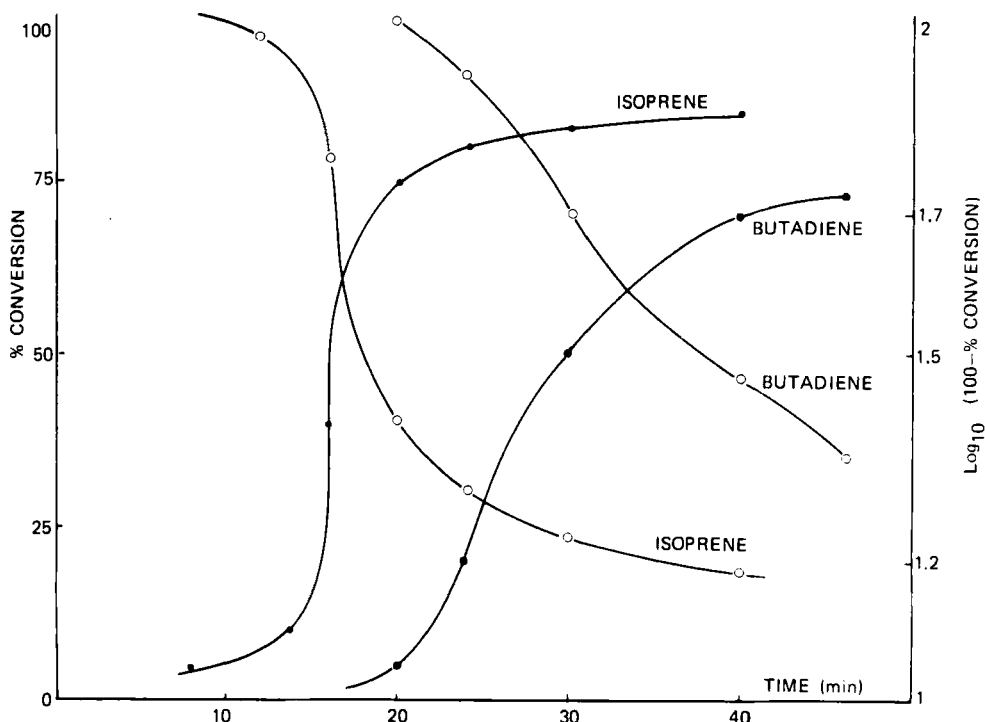


FIG. 1. Typical plot of % conversion and $\log(100\% \text{ conversion})$ vs time at 20°C . $[\text{Monomer}] = 100 \text{ mmol}$, $[\text{BuLi}] = 2 \text{ mmol}$, $[\text{211}] = 2 \text{ mmol}$. 20°C . (●) % conversion, (○) $\log(100\% \text{ conversion})$.

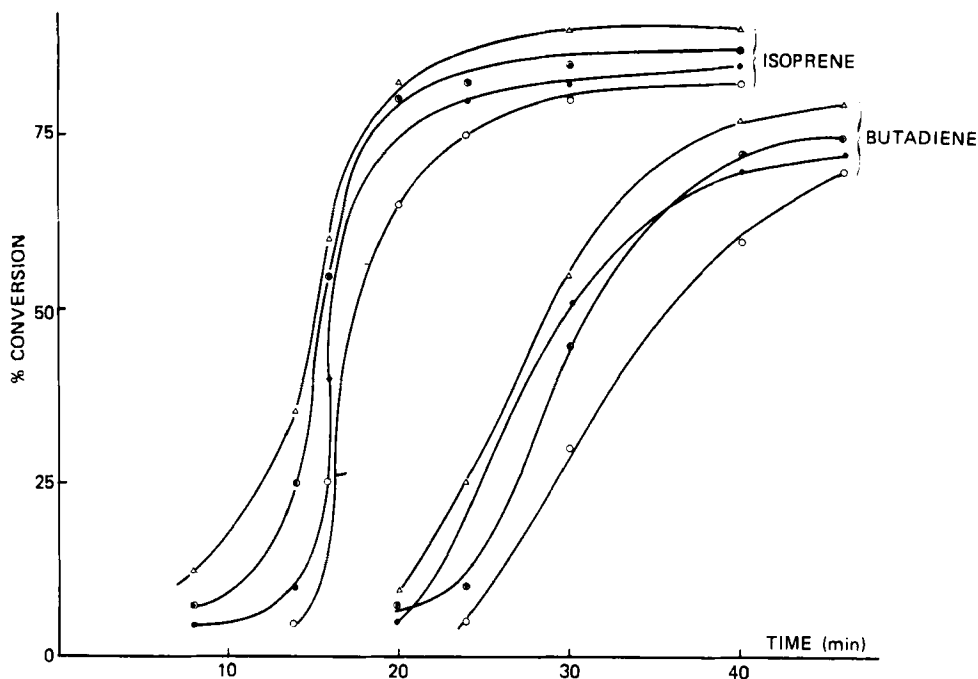


FIG. 2. Influence of the monomer concentration on the rate of polymerization: (\circ) 50 mmol, (\bullet) 100 mmol, (\odot) 200 mmol, (\triangle) 300 mmol. $[\text{BuLi}] = 2 \text{ mmol}$, $[\text{211}] = 2 \text{ mmol}$. 20°C .

The effects of the monomer concentration, of the cryptant concentration, of the counterion, and of the (initiator)/(cryptant) molar ratio on the induction period and the microstructure of the polymer produced could be systematically investigated.

Variation of Induction Period, Molecular Weight, and Microstructure with Monomer Concentration

Investigations at a variety of different monomers and monomer concentrations demonstrated that no simple relationship exists between the overall induction period and the monomer concentration. However, representative results are shown in Fig. 2 which demonstrate that the induction period increase when the monomer concentration decreases. Nevertheless, the induction periods were longer than in the case of MMA. It is obvious that solvation of the initiator by the monomer, which promotes complexation and solubilization, is slower.

TABLE 1. Influence of Monomer Concentration

Monomer (mol)	Yield (%)	\bar{M}_n^a	Microstructure (%)			
			1-4	1-2	3-4	
Isoprene	300	80	35,000	30	20	50
	200	85	29,000	27	21	52
	100	85	17,000	30	19	51
	50	90	20,000	25	21	54
	25	85	15,000	27	20	53
Butadiene	300	65	9,400	35	65	
	200	80	7,300	37	63	
	100	70	7,000	40	60	
	50	80	5,400	36	64	
	25	70	5,000	37	63	

^a Measured by VPO at 37° in toluene; BuLi = 2 mmol; 211 = 2 mmol; 20° C; polymerization time = 40 min.

The molecular weight of the polymer produced was found to be more or less independent of the monomer concentration in the concentration range investigated (Table 1) and was higher at the theoretical value. On the other hand, the monomer concentration has no influence on the relative proportions of the possible polyadditions, especially if 1-2 and 3-4 additions are observed (Table 1).

Variation of Induction Period, Molecular Weight, and Microstructure with (Initiator)/(Cryptant) Molar Ratio

The effect of varying the cryptant (211) concentration on the overall rate of polymerization was studied at 20° C with isoprene and butadiene as monomers.

The experimental results depicted in Table 2 show that initially the rate of polymerization rapidly increases with an increase in cryptant concentration, and reaches a maximum value when the ratio (initiator)/(cryptant) is equal to one. However, we notice that the induction period is longer in the case of butadiene than in the case of isoprene and much longer than for MMA [14].

On the other hand, we notice (Table 2) that 1-4 addition slowly increases when the cryptant concentration decreases, tending to the

TABLE 2. Influence of the (211)/(BuLi) Molar Ratio

Monomer (211)/(BuLi)	Yield (%)	\bar{M}_n^a	Microstructure			
			1-4	1-2	3-4	
Isoprene	1	75	15,000	30	19	51
	0,8	70	14,500	32	18	48
	0,6	65	12,500	35	16	49
	0,4	60	12,000	39	15	46
	0,2	58	10,000	45	16	39
	0,1	50	9,700	57	14	29
	0	35	7,000	92	6	2
Butadiene	1	70	7,000	40	60	
	0,8	65	6,700	42	58	
	0,6	62	6,400	44	56	
	0,4	57	5,900	47	53	
	0,2	50	5,300	50	50	
	0,1	43	4,800	60	40	
	0	20	3,000	92	8	

^a Measured by VPO at 37°C in toluene; monomer = 100 mmol; BuLi = 2 mmol; 20°C; polymerization time 40 min with butadiene and 10 min with isoprene.

value observed with BuLi alone. In addition, as in solution polymerization, the presence of cryptant essentially leads to 1-2 and 3-4 additions. Nevertheless, the percentage of 1-4 addition is more important in bulk polymerization.

Finally, we notice that the molecular weight is slowly affected by the (BuLi)/(221) ratio (Table 2).

Variation of Induction Period and Microstructure with Temperature of Polymerization

The variation in the overall rate of the polymerization induction period and microstructure with BuLi-211 as initiator is shown in Table 3 and Fig. 3. The lower polymerization rate and the longer induction period observed at lower temperatures may be reasonably attributed to a heterogeneous system.

TABLE 3. Influence of Temperature, Cryptant Nature, and Organo-lithium Compound

Monomer	Initiator	θ (°C)	Yield (%)	\bar{M}_n^a	Microstructure		
					1-4	1-2	3-4
Butadiene	BuLi-211	20	70	7,000	40	60	
		0	65	9,200	39	61	
		-20	62	6,900	37	63	
		-40	60	7,500	39	61	
		-78	50	7,100	40	60	
	BuLi-221	20	70	8,200	40	60	
	BuLi-222	20	75	9,400	45	55	
	MeLi-211	20	80	8,300	40	60	
	PhLi-211	20	70	6,700	39	61	
	Isoprene	BuLi-211	20	85	17,000	30	19
0			80	16,500	32	20	48
-20			78	18,000	30	19	51
-40			68	17,400	31	19	50
-78			55	12,000	30	20	50
BuLi-221		20	80	16,000	30	19	58
BuLi-222		20	85	21,000	35	18	46
MeLi-211		20	80	18,400	32	17	51
PhLi-211		20	87	23,100	31	20	51

^a Measured by VPO at 37°C in toluene; monomer = 100 mmol; initiator = 2 mmol; cryptant = 2 mmol; polymerization time = 10 min.

However, it was possible to initiate bulk polymerization of diene monomers with cryptants at lower temperature, but the natures of the polymers formed do not vary and vinyl addition is preferentially observed.

Variation of Induction Period and Microstructure with the Nature of the Cation

It is well known that 1-4 addition increases in nonpolar solvents with an increase of the counterion in the case of isoprene [12] but does not vary with butadiene [17].

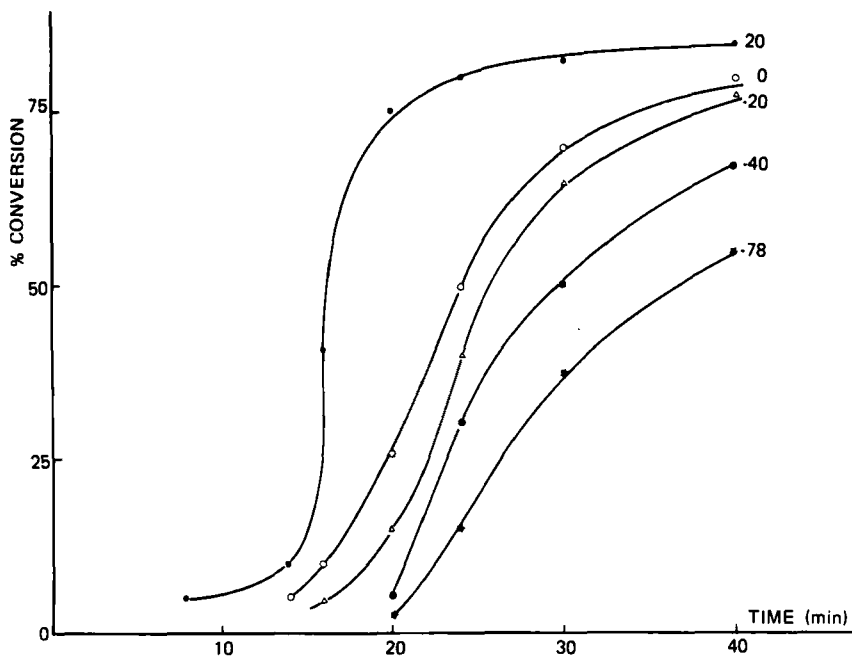


FIG. 3. Influence of the temperature on the rate of isoprene polymerization: (●) 20°C, (○) 0°C, (△) -20°C, (⊙) -40°C, (★) -78°C. [BuLi] = 2 mmol, [211] = 2 mmol, [isoprene] = 100 mmol.

The polymers obtained with Li, Na, K, Rb, and Cs as counterions, complexed by cryptants in bulk polymerization, mostly lead to vinyl addition, and the proportions observed are roughly independent of the counterion (Table 4).

We notice that the induction period varies with the counterion and the rate of polymerization increases with the size of the counterion (Fig. 4).

Variation of Microstructure with Initiator Nature and Cryptant Nature

Different cryptants were chosen with organolithium compounds. The microstructures obtained are gathered in Table 3. We note that the cryptants gave different microstructures compared to the ones obtained by organolithium taken separately. The polymers obtained are mostly 1-2 and 3-4 additions and independent of the nature of the cryptant and of the organolithium compound.

TABLE 4. Influence of the Nature of the Cation

Monomer	Initiator	Yield (%)	\bar{M}_n^a	Microstructure		
				1-4	1-2	3-4
Butadiene	BuLi-211	70	700	40	60	
	Nap, Li ⁺ , 211	70	7,300	37	63	
	Nap, Na ⁺ , 221	75	10,100	35	65	
	Nap, Rb ⁺ , 222	85	9,400	34	66	
	Nap, Cs ⁺ , 222	90	8,900	34	66	
	Nap, Cs, 222	92	7,900	31	68	
Isoprene	BuLi-211	85	17,000	30	19	51
	Nap, Li ⁺ , 211	83	18,500	30	20	50
	Nap, Na ⁺ , 221	84	19,700	27	20	53
	Nap, K ⁺ , 222	90	21,500	25	23	52
	Nap, Rb ⁺ , 222	92	20,000	25	24	51
	Nap, Cs ⁺ , 222	95	24,000	23	24	57

^a Measured by VPO at 37°C in toluene; monomer = 100 mmol; initiator = 2 mmol; cryptant = 2 mmol; 20°C; polymerization time = 40 min.

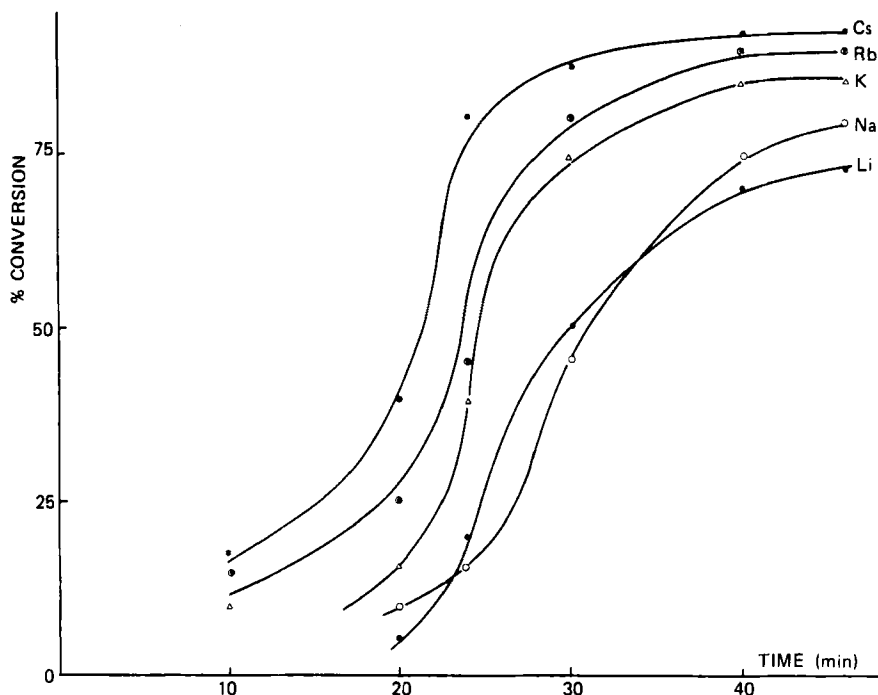


FIG. 4. Influence of the nature of the cation on the rate of butadiene polymerization at 20°C. [Butadiene] = 100 mmol, [initiator] = 2 mmol, [cryptant] = 2 mmol. Polymerization time, 20 min.

CONCLUSIONS

Any analysis of these experimental results must take into account the following characteristic features which have been established for these polymerizations.

The induction periods observed with monomer concentration, (initiator)/(cryptant) molar ratio, temperature, and counterion vary more or less.

The molecular weights observed are always higher than the theoretical value. Similar results are observed in solution polymerization with the same cryptants.

The structure of polymers produced is essentially vinyl and is roughly independent of the parameters studied here.

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