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Henry S. Makowski^a; Merrill Lynn^a; Alan N. Bogard^a

^a Esso Research and Engineering Company Linden, New Jersey

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Butyllithium Polymerization of Butadiene. II. Effects of Solvent and Temperature on Association of Polybutadienyl Lithium*

HENRY S. MAKOWSKI, MERRILL LYNN, and ALAN N. BOGARD

*Esso Research and Engineering Company
Linden, New Jersey*

SUMMARY

In the butyllithium polymerization of butadiene in aliphatic solvents at 25°C, the first few monomer units are incorporated largely in a 1,2 manner. With increasing degree of polymerization the extent of 1,2 addition decreases to a limiting value of about 10% at a degree of polymerization of about 50. However, within this region of high 1,2-addition increasing solvent basicity, i.e., changing from aliphatic to aromatic solvents, markedly reduces extent of 1,2 addition and also narrows the molecular weight distribution. Further, in aliphatic solvents, increasing polymerization temperature from 25 to 60°C also results in a marked reduction in 1,2 addition. These results are consistent with the concept that an ion pair of the associated organolithium complex, $[R_{(n-1)}Li_n]^{\oplus}R^{\ominus}$, is the active polymerization species and that changes in mode of monomer incorporation are due to changes in the degree of association of the entire organolithium system.

INTRODUCTION

In an earlier paper [1] it was demonstrated that, in the polymerization of butadiene with butyllithium in hydrocarbon solvents, degree

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of association (DA) of the organolithium species changes rapidly with increasing degree of polymerization from a value of n for the initiator to a limiting value of 2. More significantly, however, the degree of association at first increases to a very high level and then almost as rapidly decreases with further increase in degree of polymerization. These changes in association coincide with changes in polybutadiene microstructure, i.e., in the stereochemical course of the polymerization. Based on this and other observations, it was concluded that changes in degree of association were responsible for changes in microstructure and that the associated organolithium partakes directly in monomer insertion.

It was further shown that increasing temperature tends to dissociate higher-order agglomerates, whereas lower-order agglomerates (DA = 2) are relatively unaffected. Ziegler et al. [2] showed that very low molecular weight polybutadienes can be varied in microstructure by varying polymerization temperature. We believe this change in microstructure to be related to the effect of increased temperature lowering the degree of association of the highly associated agglomerates. Other results have been reported on the effects of changes in hydrocarbon solvent and in temperature on initiation, molecular weight, and microstructure [3-5].

This paper is concerned with more detailed effects of temperature and solvents on the properties of low molecular weight polybutadienes and the relationship of these effects to associative phenomena in organolithium polymerization.

EXPERIMENTAL

Starting Materials

Butadiene (The Matheson Co., C.P. grade) was passed through a 3-ft column packed with calcium sulfate or barium oxide and condensed into a dropping funnel.

n-Butyllithium was obtained in hexane and heptane solvents from the Foote Mineral Co.

Heptane (Phillips Petroleum Co., pure grade), benzene (Matheson, Coleman & Bell), toluene (J. T. Baker Co., reagent grade), and mesitylene (Enjay Chemical Co.) were treated with sodium ribbon and stored under nitrogen prior to use.

Natural Attapulugus clay (200/up mesh RVM) was obtained from the Minerals & Chemicals Philipp Corp.

Analytical Methods

Kinematic viscosities of liquid polybutadienes were determined at 25°C according to ASTM 445.

Number-average molecular weights of polybutadienes were determined in benzene solutions with a Mechrolab vapor-pressure osmometer.

Densities of polybutadienes were determined at 25°C with a modified, graduated 5-ml volumetric flask.

Polybutadiene microstructures were calculated from the peaks of maximal absorption appearing around 11.0 μ (type I unsaturation), 10.4 μ (type II trans unsaturation), and 13.5 μ (type II cis unsaturation) as previously described [1].

Solvent Studies

n-Butyllithium in heptane was used as received for the heptane solvent runs. In all other cases the n-butyllithium solutions were prepared as follows: n-Butyllithium in hexane was carefully stripped under reduced pressure (2 mm Hg) and under nitrogen. Temperature during stripping was not permitted to exceed 30°C. The residual n-butyllithium was kept at full vacuum for 4 hr. The neat n-butyllithium was then diluted with dry solvent (benzene, toluene, or mesitylene) under nitrogen. The resultant solutions were analyzed for total base by the titration of aliquots with standard HCl solutions.

A series of 17 runs of varying degree of polymerization (from 3 to 100) was made with each of the four solvents at 25°C. Polymerizations were conducted in round-bottomed flasks at atmospheric pressure as described previously [1]. In every case the total volume of solvent was maintained at 1 liter. Dry butadiene (108 g, 2.0 moles) was condensed into an addition funnel, and the liquid butadiene was added to the butyllithium solution over a period of 1 hr. Polymerizations were maintained at 25 \pm 3°C. The polymerization solutions were then stirred for 16-66 hr. Polymer solutions were worked up by adding thereto 25 g of natural Attapulugus clay per 0.1 mole of starting butyllithium. The mixture was stirred vigorously for a few minutes, and the slurry filtered. The clear, colorless solutions were vacuum-stripped, and the polybutadiene residues were kept at a temperature of 100-110°C for 2 hr at 2-4 mm Hg to ensure solvent removal. The polybutadienes were filtered through Celite before being sampled for analysis. Number-average molecular weight, type unsaturation, kinematic viscosity, and density were determined on each polybutadiene.

A series of 17 runs was made in heptane solvent at 60°C as described above; however, stirring times were limited to 4 hr.

Yields and polybutadiene properties are given in Table 1.

Rate Studies

The conversion of butadiene with time was determined at three temperatures (40, 60, and 80°C) in two solvents (heptane and toluene).

Table 1. Preparation and Properties of Polybutadienes Derived from n-Butyllithium in Various Solvents

	3	5	7.5	10	12	14	16	18	20	25	30	40	50	60	70	80	100
Theoretical DP	0.667	0.400	0.253	0.200	0.167	0.150	0.125	0.111	0.100	0.080	0.067	0.050	0.040	0.0335	0.0286	0.025	0.02
n-Butyllithium, moles	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Butadiene, moles	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000	1000
Total solvent, ml	220	328	463	598	706	814	922	1030	1138	1408	1676	2218	2756	3298	3838	4378	5458
Kinetic mol. wt.																	
<u>Heptane at 25°C</u>																	
Yield, g	107.1	98.8	97.8	103.0	93.1	93.6	92.6	80.5	94.2	91.9	97.0	89.6	89.2	84.5	81.8	—	71.7
Number-average mol. wt.	390	480	645	760	780	850	980	990	1200	1320	1460	1830	2190	2210	2770	—	3570
Kinematic viscosity, stokes	0.178	0.323	0.713	0.997	1.12	1.26	1.67	1.65	1.90	3.00	3.73	6.06	9.13	10.8	14.7	—	79.5
Density, g/cc	0.8358	0.8463	0.8582	0.8627	0.8653	0.8659	0.8703	0.8701	0.8707	0.8772	0.8795	0.8815	0.8841	0.8854	0.8871	—	0.8871
<u>Microstructure</u>																	
1, 2, %	44.1	40.7	36.5	33.8	32.2	31.3	29.4	27.9	27.4	23.5	21.7	18.1	14.2	12.4	11.8	—	9.2
1, 4-cis, %	22.7	23.8	25.9	26.7	27.5	28.0	28.7	29.5	29.7	31.2	32.4	34.5	36.5	37.3	37.7	—	39.2
1, 4-trans, %	33.2	35.5	37.6	39.5	40.3	40.7	41.9	42.6	42.9	45.3	45.9	47.4	49.3	50.3	50.5	—	51.5
<u>Heptane at 60°C</u>																	
Yield, g	108.3	101.2	96.9	106.4	104.8	102.4	104.7	111.1	102.3	108.4	104.2	101.7	104.0	106.6	102.5	105.4	105.0
Number-average mol. wt.	465	540	650	840	930	1040	1120	1140	1115	1180	1280	1520	2180	2370	2650	2220	2480
Kinematic viscosity, stokes	0.237	0.39	0.58	1.07	1.42	1.75	2.07	2.59	2.78	4.16	4.97	9.29	13.4	18.5	27.2	40.5	53.7
Density, g/cc	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
<u>Microstructure</u>																	
1, 2, %	26.4	25.3	20.1	20.8	19.7	17.9	15.7	15.0	14.4	13.1	11.5	10.6	10.2	9.9	9.7	9.8	9.4
1, 4-cis, %	31.9	32.0	32.9	32.2	33.2	33.7	34.8	35.1	35.5	37.0	36.0	35.5	36.6	37.5	37.1	36.8	38.2
1, 4-trans, %	41.7	42.7	47.0	46.9	47.0	48.4	49.5	49.9	50.1	49.9	52.4	53.9	53.1	52.6	53.2	53.4	52.3

Benzene at 25°C

Yield, g	78.2	95.5	36.8	95.5	97.6	90.9	94.0	73.3	87.0	84.9	86.3	71.7	80.9	76.9	91.2	72.5	96.0
Number-average mol. wt.	300	380	320	685	730	820	1080	910	1190	1195	1590	4260	2120	2980	3460	3260	5190
Kinematic viscosity, stokes	0.066	0.116	0.073	0.534	0.583	0.793	1.39	1.00	1.80	2.26	2.88	58.3	7.06	19.3	26.7	24.0	66.1

Density, g/cc

0.8207	0.8339	—	0.8623	0.8630	0.8674	0.8730	0.8715	0.8755	—	0.8800	—	0.8853	0.8889	0.8890	—	—	—
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Microstructure

1,2, %	38.6	31.4	26.6	20.2	18.9	19.8	17.5	14.8	16.6	12.3	11.8	12.6	11.5	11.8	11.1	10.9	11.2
1,4-cis, %	25.4	28.4	31.5	32.3	33.5	32.8	34.6	36.6	34.5	37.5	37.0	37.2	37.5	37.5	38.4	38.2	38.2
1,4-trans, %	36.0	40.3	41.9	47.5	47.6	47.4	47.9	48.6	48.8	50.3	51.2	50.2	51.0	50.7	50.5	50.9	50.6

Toluene at 25°C

Yield, g	104.0	109.2	95.7	101.3	97.6	95.5	88.7	103.7	105.2	97.5	105.0	86.9	88.5	101.1	95.7	102.2	103.4
Number-average mol. wt.	300	360	480	620	670	745	835	980	1070	1170	1770	2200	2000	2630	3010	3760	3740
Kinematic viscosity, stokes	0.067	0.106	0.237	0.427	0.522	0.584	0.840	1.16	1.44	1.65	3.40	7.01	5.47	10.1	14.9	25.2	51.1

Density, g/cc

0.8206	0.8320	0.8490	0.8592	0.8630	0.8611	0.8690	0.8730	0.8746	0.8768	0.9004	0.8857	0.8831	0.8859	0.9052	0.8887	0.8893	0.8893
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Microstructure

1,2, %	36.9	30.6	23.3	19.3	17.2	16.2	14.9	13.8	13.3	12.2	12.1	11.6	11.2	11.3	11.2	11.1	10.8
1,4-cis, %	26.5	29.0	32.8	35.0	36.4	36.7	38.2	39.0	37.5	38.3	38.9	38.9	39.4	39.1	39.3	39.6	39.6
1,4-trans, %	36.6	40.2	43.9	45.7	47.4	47.1	47.0	47.2	49.2	49.5	49.1	49.5	49.4	49.6	49.6	49.3	49.6

Mesitylene at 25°C

Yield, g	91.0	112.2	85.4	92.0	103.0	104.5	103.0	93.7	101.8	101.2	96.4	107.3	103.3	102.2	99.6	103.0	96.6
Number-average mol. wt.	310	375	520	620	665	790	860	1010	990	1260	1440	2290	3070	2370	3385	3092	3980
Kinematic viscosity, stokes	0.069	0.119	0.290	0.428	0.479	0.783	0.853	1.63	1.11	1.86	2.55	7.95	33.5	11.3	20.5	30.1	57.0

Density, g/cc

0.8230	0.8344	0.8526	0.8593	0.8615	0.8677	0.8695	0.8795	0.8730	0.8764	0.8803	0.8878	0.8921	0.8861	0.8884	0.8880	0.8901	0.8901
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Microstructure

1,2, %	31.0	27.4	23.4	17.0	16.5	17.0	16.7	14.1	14.4	12.6	12.1	11.5	11.8	11.2	11.2	13.1	11.1
1,4-cis, %	28.9	30.2	32.3	35.3	34.9	35.2	35.2	36.5	36.0	37.9	37.8	38.8	38.5	38.7	39.0	37.9	39.0
1,4-trans, %	40.2	42.4	44.3	47.7	48.5	47.8	48.1	49.4	47.6	49.4	50.0	49.8	49.7	50.2	49.8	48.9	49.9

In all cases, the molar ratio of butadiene/butyllithium was kept at about 30, and the butadiene concentration at about 15 wt. %.

The polymerizations were conducted under nitrogen in glass apparatus at atmospheric pressure. The temperature of the reactions was controlled to $\pm 2^\circ\text{C}$ by a thermocap relay and a pneumatic table. The polymerization apparatus consisted of a four-necked flask equipped with an air stirrer, a thermometer well, a dry ice cold finger condenser, a dropping funnel for the addition of the catalyst solution, a dropping funnel for the addition of solvent, and a dropping funnel for the addition of monomer. The monomer funnel was equipped with a dry ice cold finger condenser for the condensation of gaseous butadiene.

Solvent and butyllithium solution were transferred to the reaction flask and heated to the desired reaction temperature. Liquid butadiene was added to the flask incrementally over a period of 1 hr and allowed to react for an additional 4 hr. At the termination of the reaction the polymerization solution was yellow in toluene and dark orange in *n*-heptane.

Samples were removed from the reaction flask (0, 30, 60, 90, 120, 180, and 240 min after the addition period) by nitrogen pressure and collected in flasks containing methanol in order to terminate the reaction. The solutions immediately lost color upon contact with methanol.

The solvent was removed by stripping under reduced pressure. Final stripping was accomplished at full vacuum (usually 2 mm Hg) and 100°C for 2 hr. Lithium methoxide was removed by filtration. Celite was added to the polymer, mixed thoroughly, and filtered through a sintered glass funnel. The polymers thus prepared were clear and colorless liquids.

The results of these runs are given in Table 2.

RESULTS

The effects of solvent type and temperature were measured primarily from polybutadiene microstructures and relative molecular weight distributions. The latter were obtained by correlations of number-average molecular weights with bulk viscosities. The effects of solvent and temperature on polybutadiene microstructure could be discerned in the molecular weight region below about 2000, where it had already been shown that with aliphatic solvents at ambient temperature polybutadienes high in 1, 2 addition are obtained [1].

The effect of solvent type on polybutadiene microstructure at a polymerization temperature of 25°C is illustrated in Fig. 1. At molecular weights below about 2000 the extent of 1, 2 addition is high in heptane but markedly reduced in the aromatic solvents. Further,

Table 2. Effect of Solvent and Temperature on Butadiene Conversion

Solvent	Heptane					Toluene								
Temperature = 40°C														
Conversion	0	30	60	90	120	180	240	0	30	60	90	120	180	240
Time after addition period, min	5.2	19.7	38.9	55.2	67.5	—	86.3	—	80.9	91.6	96.7	98.0	99.8	100
Yield, %	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Polymer properties														
Number-average mol. wt.	—	945	1090	1290	1280	1420	1460	920	1250	1990	1500	1500	1570	1600
Viscosity, stokes	—	—	1.85	2.70	3.51	3.83	3.69	0.83	1.73	2.22	2.44	2.54	2.59	2.76
Polymer microstructure														
1,2, %	—	12.3	15.6	16.9	17.4	17.2	17.0	12.5	12.5	12.5	12.5	12.5	9.3	12.2
1,4-cis, %	—	37.2	35.2	35.0	34.9	34.7	34.3	37.2	35.6	37.1	37.2	37.4	38.8	37.9
1,4-trans, %	—	50.5	49.1	48.1	47.7	48.1	48.7	50.2	49.9	50.4	50.3	50.0	41.9	49.6
Temperature = 60°C														
Conversion	0	30	60	90	120	180	240	0	30	60	90	120	180	240
Time after addition period, min	74.1	—	99.7	100	99.8	100	108	90.0	95.0	101	100	100	99.9	110
Yield, %	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Polymer properties														
Number-average mol. wt.	—	1490	1260	1750	1670	1730	1780	1770	1280	1560	1510	1460	1360	1475
Viscosity, stokes	—	3.68	5.08	5.08	5.08	5.41	5.18	2.01	2.49	2.51	2.52	2.48	2.54	2.18
Polymer microstructure														
1,2, %	—	12.6	12.6	12.7	12.4	12.5	12.6	12.2	13.0	13.1	13.1	12.9	12.8	13.1
1,4-cis, %	—	36.8	36.9	36.7	36.2	37.0	36.2	37.1	35.4	36.5	36.2	36.5	37.3	36.1
1,4-trans, %	—	50.5	50.5	50.5	51.4	50.5	51.3	50.7	51.6	50.4	50.7	50.6	49.9	50.8
Temperature = 80°C														
Conversion	0	30	60	90	120	180	240	0	30	60	90	120	180	240
Time after addition period, min	—	—	96.7	96.3	97.0	88.3	97.2	100	96.6	96.0	97.8	97.9	—	100
Yield, %	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Polymer properties														
Number-average mol. wt.	—	1740	1720	1880	1770	1760	1800	1700	1620	1685	1620	1670	1785	1660
Viscosity, stokes	—	5.06	5.37	5.46	5.45	5.57	5.62	5.79	3.22	3.51	3.50	3.49	3.36	3.57
Polymer microstructure														
1,2, %	—	11.7	11.7	12.1	11.7	11.5	11.6	11.6	13.7	13.5	13.5	13.5	13.3	13.6
1,4-cis, %	—	37.5	35.9	36.1	36.0	36.8	37.5	36.9	35.8	36.6	35.6	36.6	36.1	35.8
1,4-trans, %	—	50.8	52.4	51.8	52.3	51.6	50.9	51.5	50.5	49.9	50.9	50.0	50.7	50.5

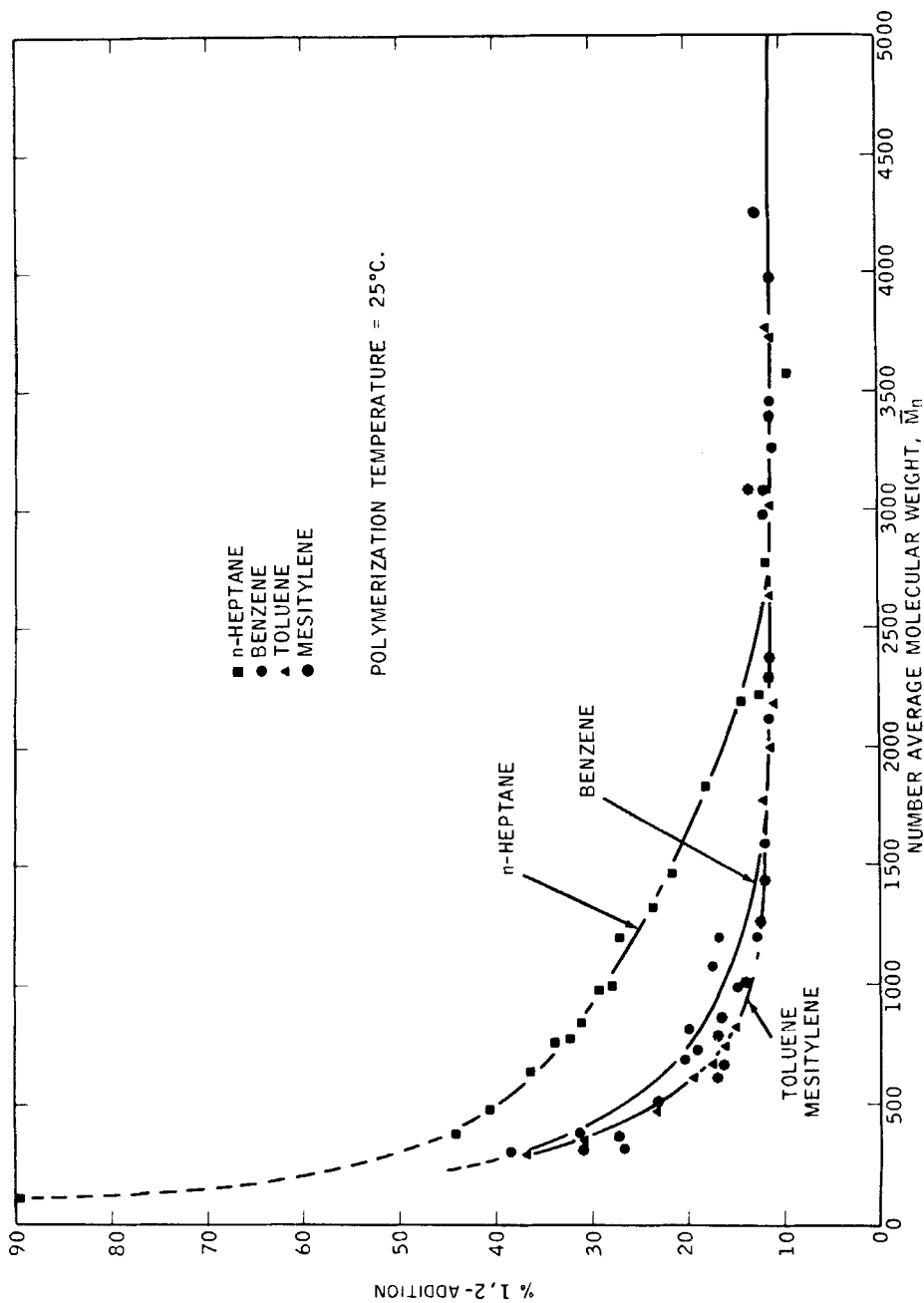


Fig. 1. Effect of solvent on polybutadiene microstructure.

although the differences are small, it appears that benzene is less effective in this regard than toluene and mesitylene, which are equivalent. In heptane an increase in polymerization temperature to 60°C also reduces 1,2 addition to about the same level obtained with aromatic solvents at 25°C. This temperature effect is illustrated in Fig. 2. After a molecular weight of about 2000-2500 has been achieved, the microstructures of the polybutadienes are the same regardless of polymerization solvent and temperature.

The data in Table 1 show that as molecular weight increases cis-1,4 addition increases somewhat faster than the trans-1,4 addition, both at the expense of 1,2 addition. Thus a polybutadiene of 400 molecular weight prepared in heptane solvent at 25°C has a cis/trans ratio of 2:3, while the polybutadienes with molecular weights above 2500 have cis/trans ratios of about 4:5.

The relationships of bulk viscosity to number-average molecular weight for polybutadienes prepared in four different solvents are given in Fig. 3. The curves in this figure are the best fit of the data from each solvent system for the equation

$$\eta = K' \bar{M}_n^a \quad (1)$$

A statistical analysis of all the data showed that the $\eta - \bar{M}_n$ curve for heptane is different from those of the aromatic solvents, i.e., benzene, toluene, and mesitylene. Within the limits of experimental error all the data from the benzene, toluene, and mesitylene systems are indistinguishable and hence can be described by a single curve. The significant point is that the bulk viscosities of polybutadienes prepared in heptane are higher than those of polybutadienes prepared in aromatic solvents at any given number-average molecular weight. These differences in bulk viscosity cannot be attributed to microstructure effects if for no other reason than that these differences persist to molecular weights where polybutadiene microstructures are identical. Thus solvents, in addition to affecting polybutadiene microstructure, also affect molecular weight distribution. Molecular weight distribution in turn is related to relative rate of initiation.

Although the difference in bulk viscosities persist to higher molecular weights, only the data for $\bar{M}_n \leq 1500$ (cf. Fig. 3) were included in the analysis, since number-average molecular weight determinations are more accurate at lower molecular weight [6] and since the breadth of molecular weight distribution due to initiating effects should be most noticeable at lower molecular weights.

For all the polybutadienes reported herein the value of a in Eq. (1) is constant [7] independent of polymerization solvent, since

$$\eta = K \bar{M}_w^a = K(D\bar{M}_n)^a = K D^a \bar{M}_n^a = K' \bar{M}_n^a \quad (2)$$

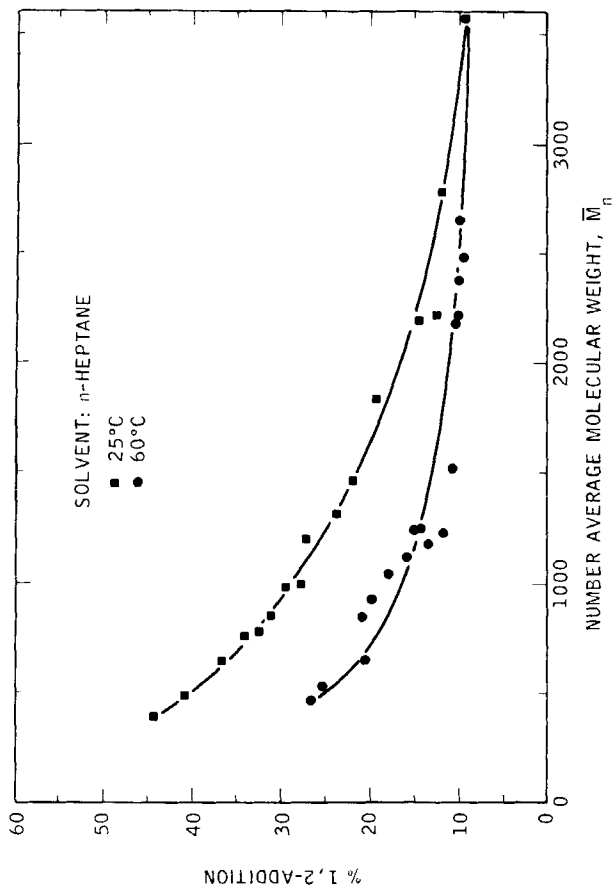


Fig. 2. Effect of temperature on polybutadiene microstructure.

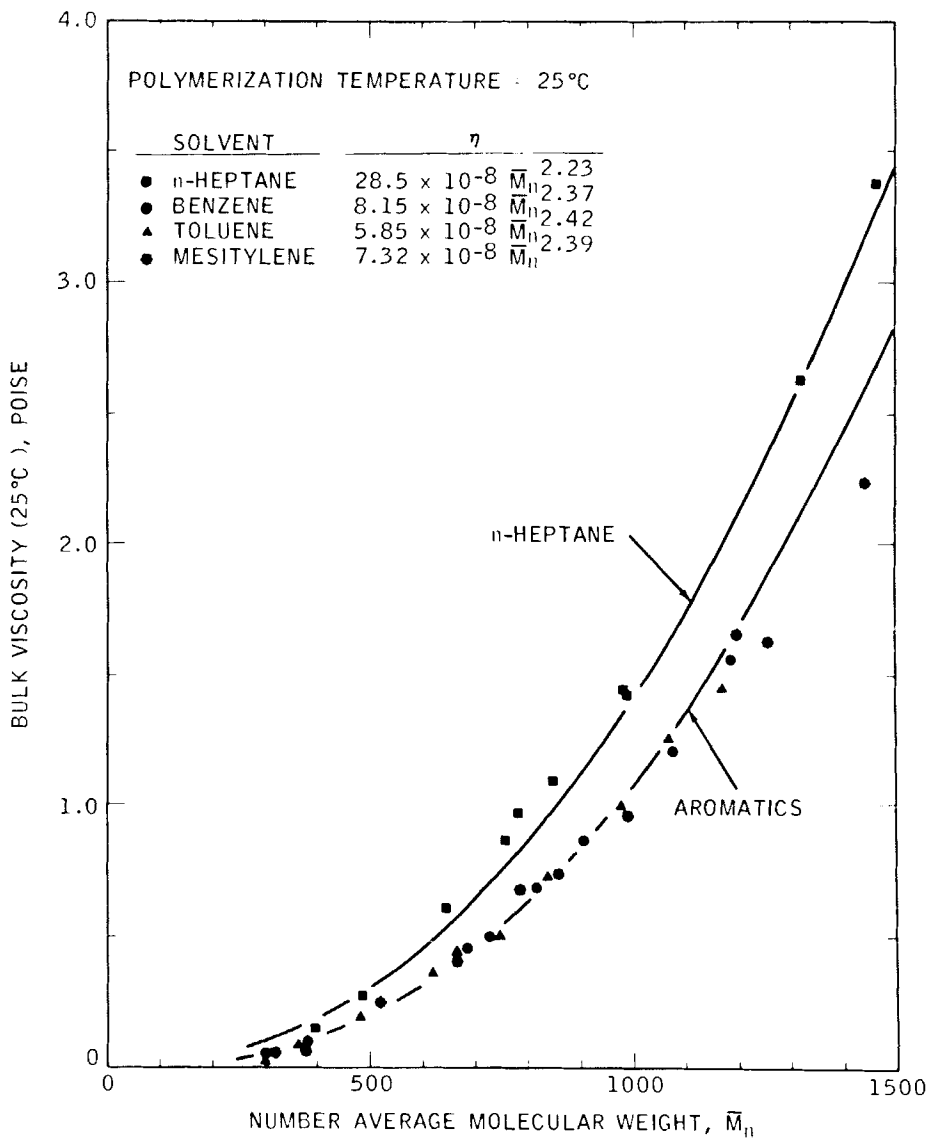


Fig. 3. Effect of solvent on polybutadiene molecular weight distribution.

where $D = \bar{M}_w/\bar{M}_n$. The average value of a for the four solvent systems was found to be 2.35 ± 0.09 . The magnitude of the deviations due to experimental error for the average and individual values of a justify the use of an average value of a to describe the molecular weight-bulk viscosity behavior of all the polybutadienes. Thus, since a can be considered constant in these systems, differences in molecular weight distribution should be reflected directly in the individual values of K' . However, even for the molecular weight range examined herein, K' itself most likely is not truly constant, since the relatively large \bar{M}_w/\bar{M}_n at low molecular weights due to initiating effects is expected to decrease with increasing molecular weight. An evaluation of the constancy of K' might best be accomplished via gel permeation chromatography on a molecular weight series of polybutadienes, since molecular weight distribution is obtained directly.

An increase in polymerization temperature, which resulted in a change in polybutadiene microstructure, surprisingly had no determinable effect on the bulk viscosities of polybutadienes (cf. Table 1).

The effects of solvent and temperature on polymerization rate are detailed in Table 2 and illustrated in Fig. 4. In these studies butadiene was added incrementally over a period of 1 hr. This was necessary to achieve reasonable temperature control. Thus the zero times in Fig. 4 represent the times at which all butadiene had been added. A significant point in this figure is that at 40°C the heptane conversion curve is S-shaped while the toluene conversion curve is less S-shaped in character (if S-shaped at all).

This can be interpreted in terms of "initiating" effects, i.e., continued "initiation" of polymer chains over a longer portion of reaction time. This also explains the difference in molecular weight distributions of polybutadienes prepared in each of these solvents.

Additional information on initiating effects is illustrated in Fig. 5. Under the conditions described herein it is seen that, even at low \overline{DP} with total monomer conversion, a polymer chain is formed for every initiator molecule present. With benzene and toluene solvents total initiation is attained at \overline{DP} of about 5, whereas with heptane this does not occur until a \overline{DP} of 10-15.

In Fig. 6 polybutadiene density is plotted as a function of number-average molecular weight. Polybutadiene density appears to be related directly to number-average molecular weight and to be independent of microstructure. It is interesting to note that with this correlation, in the region below $\bar{M}_n = 1000$, molecular weight can be obtained through a simple density determination.

DISCUSSION

The above results are interpretable in terms of the effects of temperature and solvent on the degree of association (DA) of the

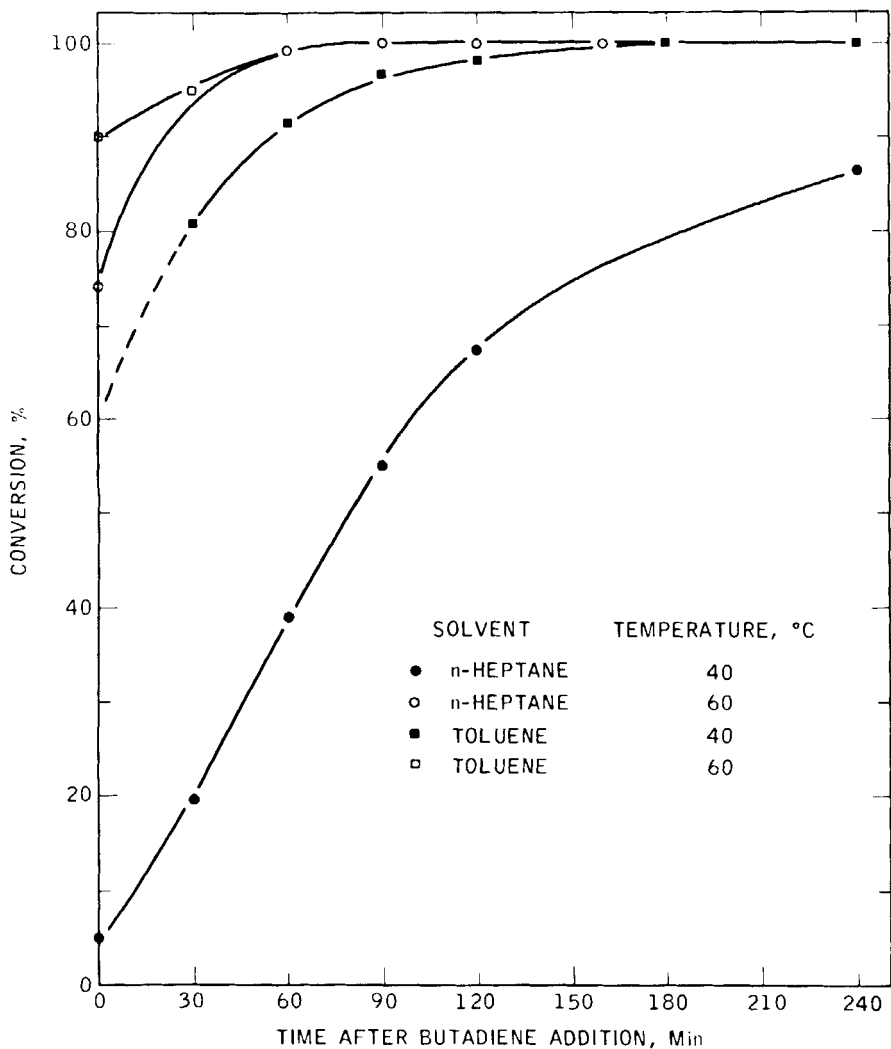


Fig. 4. Effect of solvent and temperature on butadiene polymerization rate.

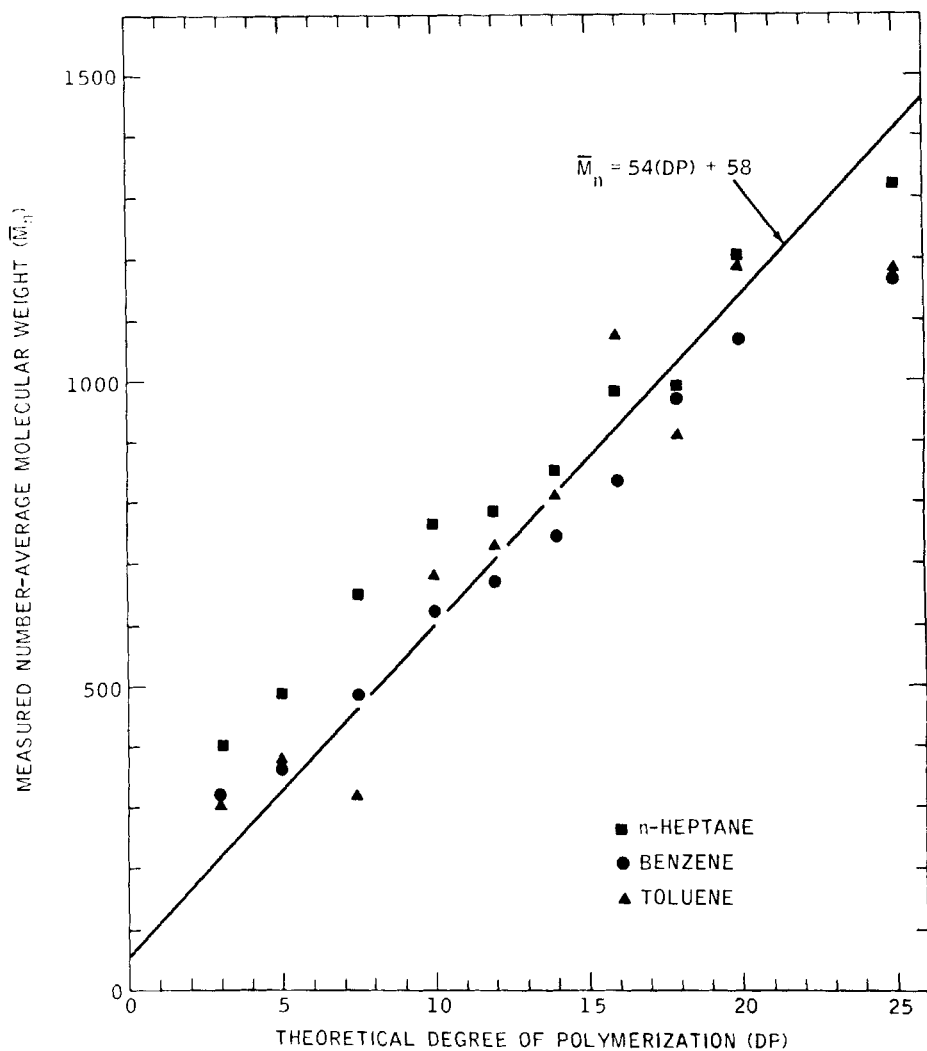


Fig. 5. Effect of solvent on initiator consumption.

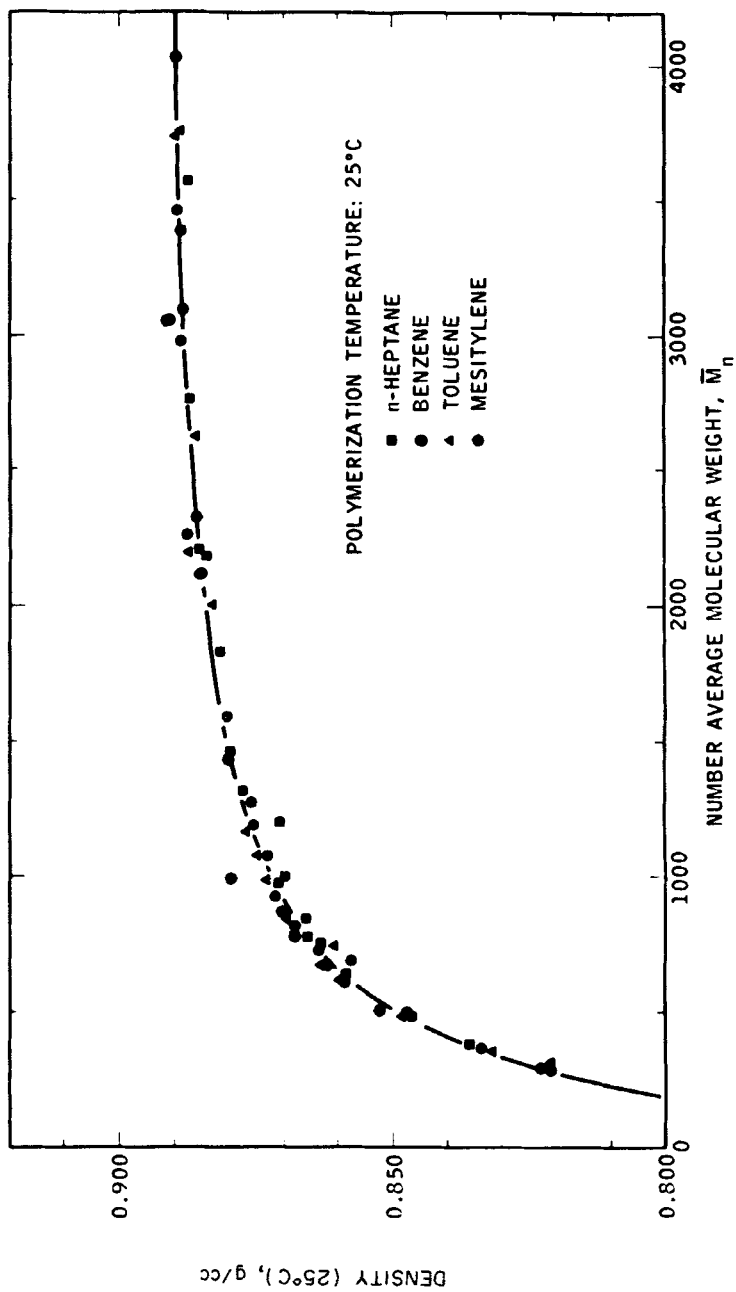
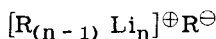


Fig. 6. Effect of number-average molecular weight on polybutadiene density.

organolithium agglomerate. As described earlier [1], the DA of the agglomerate is highest when the first few monomer units are incorporated, then drops off rapidly with increasing \overline{DP} . It is in this region of rapidly changing \overline{DA} that the solvent and temperature effects are noted. At higher \overline{DP} , where the DA has reached a limiting value of 2, no changes in polymer properties are found with changes in solvent and temperature. At this point the DA of the propagating organolithium species itself is not changed by further increases in \overline{DP} or changes in solvent and temperature. Thus these variables have no effect on the mode of monomer incorporation by this discrete organolithium species with an apparently lower limiting $DA = 2$. This is important because a logical extension of this finding is that temperature and solvent changes should not appreciably affect the mode of monomer incorporation of any discrete organolithium species, regardless of DA.

If this extension is accepted, then the effects noted at low \overline{DP} can be due only to changes in DA. It follows then that organolithium species of different DA incorporate monomers differently. This, perhaps, will not be considered unexpected but, as far as we know, this is the first direct evidence for this "expectation." Apparently, the effects of increasing solvent basicity and increasing temperature on higher-order agglomerates are simply to produce lower-order associates, e.g., $DA = 2$ earlier in the polymerization.

The nature of the polybutadiene microstructure changes at low \overline{DP} sheds some light on the nature of monomer insertion reactions at high DA. At very low \overline{DP} polybutadiene is high in 1,2 content and low (ca. 20%) in cis-1,4 content. This result is more in keeping with the concept that the active organolithium species is acting more like an ion pair than like a covalent compound [8, 9]. Thus, at least at high DA, species such as



are concluded to be active in monomer insertion.

This and earlier work tend to highlight the importance of association phenomena in organolithium polymerization. A major contribution to the understanding of the mechanism of organolithium polymerization would be the study of the effect of DA on the course of polymerization; however, the major problem here is that DA changes, and rapidly, with \overline{DP} . Ideally the effects of DA should be studied in a system where DA is kept constant under normal polymerization conditions. In theory, this is possible by coassociating the active organolithium with polymerization inactive and associated lithium compounds. Lithium salts have a demonstrable effect on microstructures of polyisoprenes and polybutadienes of higher molecular weight [10-12]. We have demonstrated that lithium compounds indeed exert a large effect on polybutadiene microstructure [13].

Probably the most extensive work on the effect of polymerization variables on polydiene microstructure and on molecular weight distribution, as well as on other properties, has been done by Hsieh [5]. His results are interesting to us because, in some instances, his results are contrary to ours. It should be pointed out, however, that Hsieh's lower molecular weight range was still about two times higher than our upper range. Consequently direct comparisons are not possible. Nevertheless, Hsieh has reported that in the butyllithium polymerization of butadiene: (1) toluene produces more 1,2 addition than aliphatic solvents, although the difference is not large (ca. 4%), (2) increasing temperature increases 1,2 addition while cis-1,4 addition remains constant, (3) at total monomer conversion increasing molecular weight increases cis-1,4 addition markedly while 1,2 addition is relatively unaffected, and (4) microstructure does not change with increasing monomer conversion. Assuming the validity of these results there are two possible general explanations, i.e., (1) a further decrease in DA at high molecular weights, and (2) incomplete "initiation."

The results of Morton and Fetters [14] would tend to show that dimeric organolithium of reasonably high molecular weight is dissociated to some extent, so that monomeric RLi could be present. An increase in molecular weight, in solvent basicity, and in temperature would tend to increase this dissociation. Monomeric RLi is expected to be different in character than dimeric RLi, so that different modes of monomer incorporation would be predicted, assuming that the ion pair $\text{RLi}_2^{\oplus}\text{R}^{\ominus}$ is the active species in dimeric RLi.

Stearns and Forman [15] suggested the possible association of initiator with polydienyl lithium to account for microstructure changes with increasing molecular weight. Hsieh has discounted this on the basis that all his initiator was consumed. However, in view of our results, this explanation can be reactivated. Total consumption of initiator does not necessarily free propagation from "initiating effects."

Neither of these possibilities totally explain Hsieh's results. However, some relatively simple experiments can be run which can shed more light on the subject. Morton et al. [16] have demonstrated that their "seeding" technique produces polymers of predicted molecular weight, whereas "normal" procedures produce polymers of higher molecular weight. Thus appropriately prepared "seeds" could be first characterized to rule out high DA and then utilized in studying properties of polydienes under different conditions (molecular weight, temperature, solvent). If initiating effects are causing the results of Hsieh, then the "seeding" technique should change these results. On the other hand, if the "seeding" technique gives the same results, it is suggested that organolithium polymerizations are even more complex than imagined today.

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