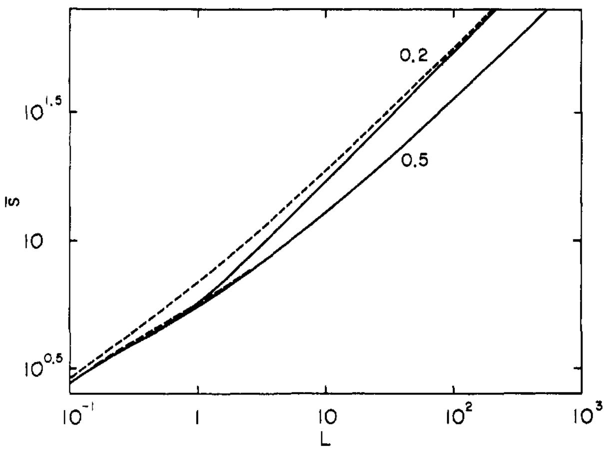

Figure 9. Double logarithmic plots of $\bar{s}$ against L for $\nu = 7$ and $d = 0.01$; see legend to Figure 7.

same $\bar{s}$ corresponding to the rod in the limit $L \to 0$. It is seen that this dependence is larger for larger ν, and also that the difference between the HW and associated KP chains in $\bar{s}$ is larger for smaller μ (for stronger helical nature) irrespective of the values of ν and is negligibly small for $\mu \gtrsim 0.5$ provided that $L \gtrsim 10$. This implies that the equation for the KP chain is valid in a good approximation for $\mu \gtrsim 0.5$ irrespective of the values of d, as mentioned already.

Finally, it is possible to make also the plots which show the dependence on ν for various values of μ with d fixed. If ν is increased at constant μ, supposing that λ is fixed, then the unreduced κ_0 and τ_0 increase at constant κ_0/τ_0, and therefore the unreduced ρ and h decrease at constant ρ/h (with the unreduced d fixed). However, such a variation of the parameters leads to no salient and systematic change of the plots, and therefore we do not show them.

Conclusion

We have presented the useful empirical formula for the translational friction and diffusion (or sedimentation) coefficients of helical wormlike cylinders on the basis of the theoretical values evaluated by the Oseen–Burgers procedure with the preaveraged Oseen tensor. The analysis of the results shows that it is difficult to determine the model parameters accurately from, for instance, sedimentation coefficients alone, and especially that certain stiff (helical wormlike) chains may exhibit the same dependence of the sedimentation coefficient of the molecular weight as flexible chains. Thus, a study of the intrinsic viscosity and also other transport coefficients of helical wormlike chains is required. It is then suggested that there is a possibility of interpreting consistently some experimental data for both the intrinsic viscosity and sedimentation coefficient on the basis of the helical wormlike chain even when the assumption of the random coil or of the wormlike model fails.

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Molecular Weight and Carbon-14 Distributions of Poly(2-alkylbutadienes) Obtained in the Presence of Bis[(π-crotyl-^{14}C)nickel iodide]

L. A. Churlyaeva, V. I. Valuev, V. S. Bodrova, T. S. Dmitrieva, M. I. Lobach, and V. A. Kormer*

S. V. Lebedev Synthetic Rubber Research Institute, Leningrad, 198035, USSR.
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ABSTRACT: The MWD and ^{14}C distribution of poly(2-alkylbutadienes) obtained in the presence of bis[(π-crotyl-^{14}C)nickel iodide] in benzene solution has been studied. It is shown that both the polymer chain length and the nature of the 2-alkyl substituent in polydiene play a decisive role in determining the dissociation degree of dimeric π-allylic active sites. The correlation between MWD and the ratio of the monomeric species of active sites to the dimeric ones is established.

In our previous study[1] we suggested that the mode of MWD of polybutadienes formed in the presence of bis(π-crotylnickel iodide) is determined not only by the "living" chain mechanism operative in this reaction but also by the recombination effects observed during the deactivation of active sites. The recombination itself is dictated, first, by the π-allylic nature of active sites and, second, by their dimeric state. The growth of the molecular weight of "living" macromolecules should favor ever increasing dimer–monomer dissociation.

The importance of the investigations of diolefine transformations catalyzed by allylic systems to the understanding of the ionic coordination catalysis encouraged us to study the polymerization of 2-alkylbutadiene homologues whose behavior in these reactions was found to have some important distinguishing features.[2]

Experimental Section

The experimental procedure used was previously described.[1] 2-Ethyl- and 2-isopropylbutadienes were prepared by pyrolysis of the corresponding 2-alkyl-3-acetoxy-1-butenes.[3] Polymerization of isoprene was carried out in a 3.0-L stainless steel autoclave at 40 °C. Polymerization of 2-ethyl- and 2-isopropylbutadienes was conducted in glass ampules at 20 °C. The number-average molecular weights of polymers and also of adducts of π-crotylnickel

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Table I
Fractionation Data for Polyisoprenes Obtained at Different Conversions[a]

sample no.	conversion, %	fraction	wt % of fraction	mol % of fraction	$\bar{M}_n$	$K = \bar{M}_w/\bar{M}_n$	n^b
1	15				1010	1.04	1.5
		1	19.2	26.1	740		1.1
		2	27.1	28.8	950		1.5
		3	13.4	12.9	1050		1.6
		4	40.3	32.2	1340		1.7
2	41				1880	1.11	1.2
		1	4.8	8.5	1070		0.7
		2	33.9	45.0	1400		0.9
		3	5.5	5.0	2070		1.2
		4	14.5	13.0	2090		1.4
		5	11.2	8.8	2390		1.6
		6	30.1	19.7	2910		1.7
3	70				2590	1.08	1.1
		1	3.2	5.8	1400		0.7
		2	10.5	15.3	1770		0.8
		3	36.0	41.9	2200		0.9
		4	12.8	11.2	2930		1.2
		5	24.0	17.7	3450		1.4
		6	13.5	8.0	4310		1.8

[a] Initial concentration: C_5H_8, 3.1 mol/L; $(^{14}C_4H_7NiI)_2$, 3.87×10^{-2} mol/L; solvent, benzene. [b] The number of crotyl groups.

Table II
Fractionation Data for Poly(2-ethylbutadiene)[a]

sample no.	catalyst concn, mol/L	fraction	wt % of fraction	mol % of fraction	$\bar{M}_n$	$K = \bar{M}_w/\bar{M}_n$	n^b
1	0.051				4060	1.08	1.0
		1	25.3	35.8	2900		0.9
		2	24.7	25.2	3980		1.0
		3	22.9	21.4	4420		0.9
		4	27.1	17.6	6300		1.0
2	0.077				3870		1.0
3	0.096				3000	1.05	1.0
		1	5.8	12.6	1230		1.0
		2	11.9	12.7	2520		1.0
		3	24.4	24.9	2640		0.9
		4	21.5	19.5	2970		0.9
		5	18.0	15.4	3170		0.9
		6	18.4	14.9	3310		0.9

[a] Initial concentration, C_6H_{10}, 5.0 mol/L; solvent, benzene. Conversion: sample 1, 54%; sample 2, 66%; sample 3, 75%. [b] The number of crotyl groups.

iodide and 2-isopropylbutadiene were measured in benzene using a Ray ebulliometer.

The fractionation of polymers by molecular weight was performed by a stepwise extraction using the procedure described previously.[1] In the course of fractionation, eight to ten fractions were separated and the molecular weight of each fraction was measured. Based on these data, the integral MWD curves were obtained and the graphical differentiation of the latter gave the differential MWD curves. However, due to minor quantities of fractions obtained and a small difference in the molecular weight of neighboring fractions, the latter were mixed and the amount of radioactive crotyl groups was measured using these mixed fractions. Results obtained are given in Tables I-III.

Results

The polymerization of isoprene in the presence of bis[(π-crotyl-^{14}C)nickel iodide] proceeds with a constant rate over the whole range of the monomer conversions (Figure 1). As in the case of butadiene,[1] an increase in the isoprene conversion is accompanied by the expected variation in the amount of radioactive labels present in macromolecules (from 1.5 to 1.1) (Table I). Simultaneously, a growth of the number-average molecular weight ($\bar{M}_n$) is observed (Figure 2).

The MWD curves based on the fractionation data for polyisoprene samples obtained at different conversions

Table III
Fractionation Data for Poly(2-isopropylbutadiene)[a]

sample no.	catalyst concn, mol/L	fraction	wt % of fraction	mol % of fraction	$\bar{M}_n$	$K = \bar{M}_w/\bar{M}_n$	n^b
1	0.12				2540	1.04	0.9
		1	31.0	41.0	1750		0.8
		2	9.3	8.3	2600		1.0
		3	59.7	50.8	2700		1.0
2	0.15				2290	1.05	1.0
		1	11.6	15.1	1720		1.0
		2	31.4	38.5	1820		1.0
		3	57.0	46.4	2740		1.0

[a] Initial concentration, C_7H_{12}, 5.0 mol/L; solvent, benzene. Conversion: sample 1, 30%; sample 2, 38%. [b] The number of crotyl groups.

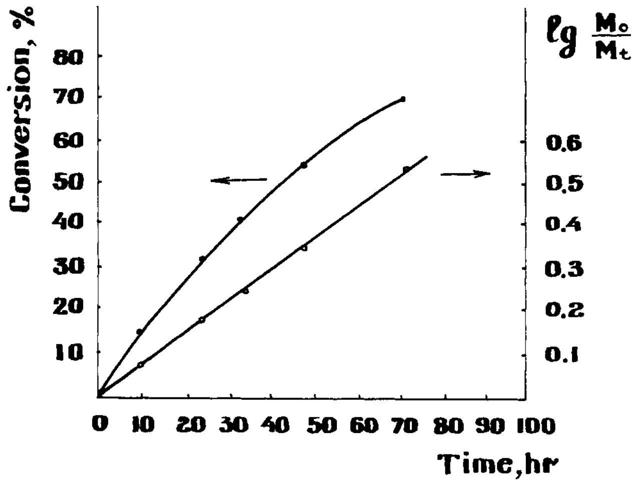

Figure 1. Kinetic curves of isoprene polymerization in the presence of bis[(π-crotyl-^{14}C)nickel iodide].

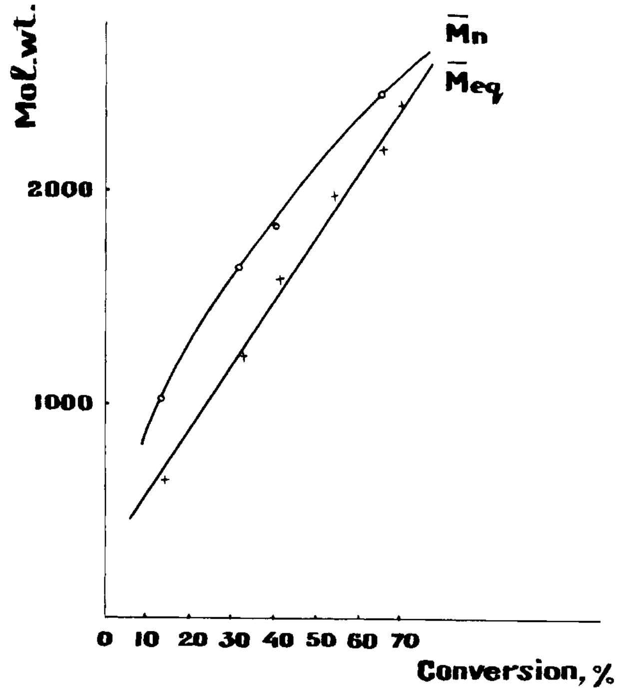

Figure 2. Dependence of number-average ($\bar{M}_n$) and equivalent ($\bar{M}_{equiv}$) molecular weight on conversion.

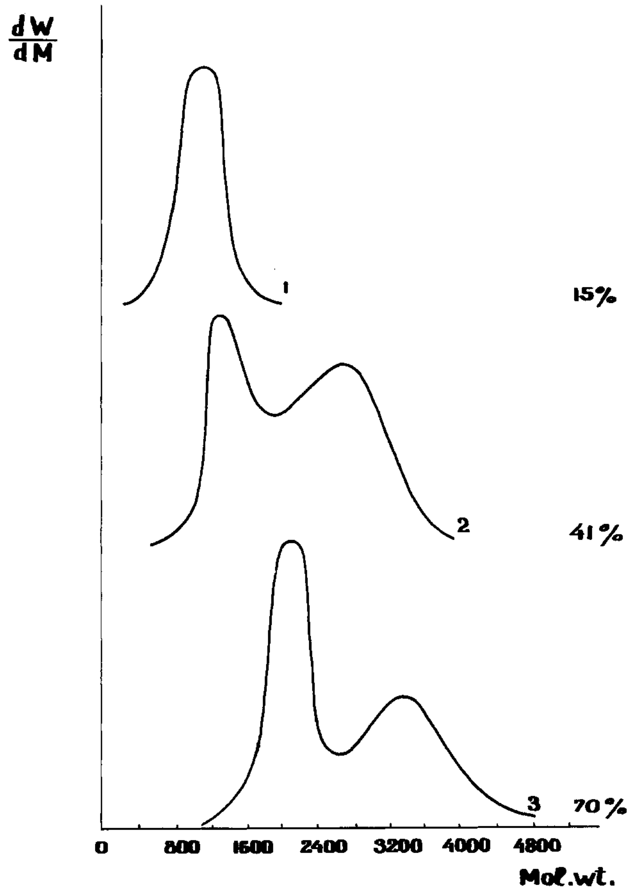

Figure 3. Differential curves of the molecular weight distribution of polyisoprenes obtained at different conversions: 1, 15%; 2, 41%; 3, 70%.

show broadening with increasing conversion and two peaks appear (Figure 3). Both peaks shift toward high molecular weights as the conversion rises. The amount of radioactive labels increases with molecular weight of the polymer fractions (Table I). The appearance of two peaks might be expected even at the early stages of transformation but the fractionation procedure failed to resolve the MWD binodality of polyisoprene with fractions differing so slightly in molecular weight.

In macromolecules of poly(2-ethylbutadienes) and poly(2-isopropylbutadienes) with number-average molecular weights greater than 1000 only one ^{14}C label is found (Tables II and III). Whatever the conversion, the MWD of these polymers is unimodal.

Discussion

The radiochemical evidence indicates unambiguously that in the presence of bis[(π-crotyl-^{14}C)nickel iodide] the polymerization of 2-alkylbutadienes similar to that of butadiene[1] exhibits all the features typical of the "living" chain mechanism. It is evident from the linear dependence of the equivalent weight ($\bar{M}_{\mathrm{equiv}}$)[1] on isoprene conversion (Figure 2) and also from the fact that there are no unlabeled chains in the polydienes.

High homogeneity of all polymers (Tables I–III) also confirms the results of previous kinetic study[2] which demonstrated that values of initiation rate constants are higher than those of propagation rate constants in the polymerizations of 2-alkylbutadienes initiated by bis(π-crotylnickel iodide).

Table IV
Molecular Weight of ^{14}C-Labeled Adducts of $^{14}C_4H_7NiI$ and 2-Isopropylbutadiene

	measured mol wt of		calcd mol wt of				
	"living" adducts	deactivated adducts	"living" adducts		deactivated adducts		
adduct			dimer	monomer	dimer	monomer	n^a
1:1	600	320	674	337	302	152	1.7
1:2	660	460	866	433	495	248	1.5
1:4	710	640	1250	625	879	441	1.2

^{a} The number of crotyl groups.

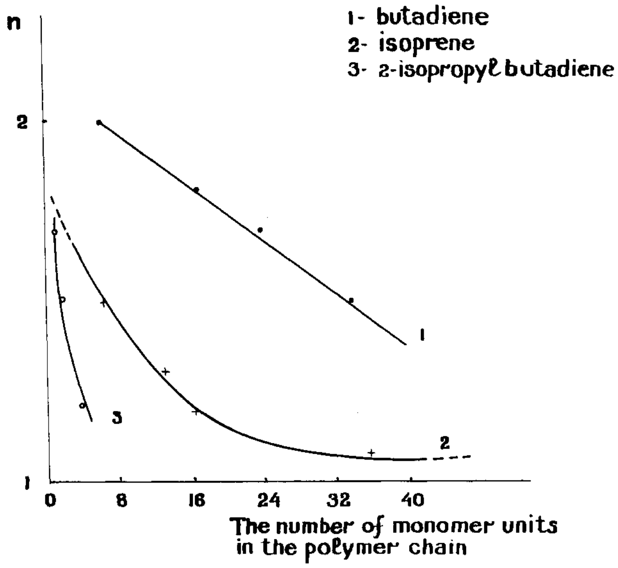

Figure 4. Change of the number of crotyl groups (n) as a function of polymerization degree: 1, butadiene; 2, isoprene; 3, 2-isopropylbutadiene.

As the conversion of isoprene rises, the curve $\bar{M}_n$ gradually straightens out, with its points approaching those of the straight line $\bar{M}_{\mathrm{equiv}}$ (Figure 2). Simultaneously, the molar portion of double-labeled macromolecules decreases in the polyisoprene fractions. These facts and binodal MWD of polyisoprene at some conversions agree well with the idea that dimerized active sites tend to undergo recombination.[1] In the present study, this idea was supported by experimental results using adducts of bis(π-crotylnickel iodide) and 2-isopropylbutadiene. The latter was chosen due to the fact that for this monomer the rate constants of the initial act of insertion exceed those of subsequent insertions to a greater extent than for other monomers within the investigated diolefine series, which allows reliable identification of 1:1 adducts. The measured and calculated molecular weights of 1:1, 1:2, and 1:4 adducts ("living" chains) and of deactivated oligomeric molecules as well as the content of radioactive labels are given in Table IV. From these data it is seen that with increasing length of the growing chain the deviation of the molecular weight of the "living" adduct from the theoretical value calculated for a dimeric species increases, the molecular weight gradually approaching that calculated for a completely dissociated adduct. The same trend is observed in the variation of the number of radioactive crotyl groups found in deactivated oligomers. The data in Table IV allow the following important conclusions to be made: the adducts of crotylnickel iodide and 2-isopropylbutadiene tend to dimerize; an increase in their molecular weight is accompanied by dissociation; deactivation of the dimerized "living" adducts results in recombination; and, finally, the variation in the number of labels present in oligomers from 2 to 1 correlates reasonably well with the number of recombined molecules (the number of radioactive labels gives a measure of the amount of associated active sites).

Comparison between the results of the present study and those obtained in investigating the polymerization of butadiene[1] indicates that the introduction of alkyl substituent into butadiene decreases the tendency of "living" macromolecules to dimerization; the same effect is observed with increasing homologue difference (Figure 4). With the number-average molecular weight of about 2000 the polybutadiene "living" chains are essentially dimeric (the amount of labels upon deactivation is 1.7), poly(isoprenylnickel iodide) is predominantly monomeric (the amount of labels is 1.2) (Table I), and the "living" chains of 2-ethyl- and 2-isopropylbutadienes are exclusively monomeric (Tables II and III). That the dissociation of poly(2-isopropylbutadienylnickel iodide), in particular, occurs at lower molecular weights is seen from the data in Table IV. The difference in the association degree between poly(butadienyllithium) and poly(isoprenyllithium) has already been reported.[4] From the foregoing it is evident that the binodal MWD will result if sufficient quantities of both the dimeric and monomeric active sites are present in the system. This is readily seen from the data on polymerization of butadiene[1] and isoprene. In the polymerization of 2-ethyl- and 2-isopropylbutadienes the active sites are dimeric only at the earliest stages of transformations, which accounts for the unimodal MWD of these polymers.

For poly(dienylnickel iodides), an increase in the dissociation degree with molecular weight can be well rationalized on the basis of generally accepted ideas of thermodynamics of polymeric systems; i.e., in good solvents, the molecular forces increasing the effective repulsion of macromolecules can weaken the nickel–iodine bridge bonds in the dimer.

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A Quantitative Analysis of Low-Density (Branched) Polyethylenes by Carbon-13 Fourier Transform Nuclear Magnetic Resonance at 67.9 MHz

D. E. Axelson, G. C. Levy,[†] and L. Mandelkern*

Department of Chemistry and Institute of Molecular Biophysics, Florida State University, Tallahassee, Florida 32306. *Received February 27, 1978*

ABSTRACT: By utilizing predetermined equilibrium magnetization conditions and the measured nuclear Overhauser enhancement factors for the appropriate carbon atoms, we have obtained the high-field carbon-13 NMR spectra of a large number of different low-density (branched) polyethylene samples. It becomes clear from this study that there is a great diversity in structure among the different samples; thus with respect to branch type and concentration there is no unique low-density polyethylene molecule since the concentration, type, and distribution of subgroups vary widely. Previously assigned resonances are used to determine the standard side-group concentrations and the long-chain branching. However, when all the observed resonances are analyzed there is an internal inconsistency among all possible combinations that should yield identical results. Thus, other branch types, such as tetrafunctional and nonlinear ones, must also be present so that all the quantitative structural information available from the spectra has not as yet been extracted. The mechanisms that have been postulated for the generation of short-chain branches will have to be modified to account for these results.

Low-density, or branched, polyethylenes prepared conventionally under high pressure are polymers of great structural complexity and versatility with respect to properties. These unusual features result from the type and concentration of the branch groups associated with a given polymer. Thus, a quantitative analysis of the branching characteristics can be useful for several important reasons. The thermodynamic, morphological, and physical properties of the polymers should depend on the kind, distribution, and concentration of the branches. Identification of the specific branches should also help in the further elucidation of the details of the polymerization mechanisms.

Carbon-13 NMR studies have the great potential, if properly employed, of being able to specifically identify a particular branch group and determine its concentration and location relative to other branches. The indirect solution methods, with their attendant assumptions in determining the long-chain branching, are avoided. Short-chain branches can be specifically identified, rather than grouped together. A series of carbon-13 NMR studies of branching in low-density polyethylene have already been reported,[1-6] and the results have been ambiguous in many respects. The problems that have been encountered, which have not always been obvious, fall into several categories. These include the independent specification of the proper pulse NMR experimental conditions, instrumental sensitivity, peak assignments, requirements for quantitative analysis, and confirmation of internal consistency among the assignments. In addition, the extraordinarily large number of different types of low-density polyethylenes, with quite different branching characteristics, that are available for study has apparently not been fully recog-

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[†] Alfred P. Sloan Research Fellow, 1975–1977; Camille and Henry Dreyfus Teacher-Scholar, 1976.

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