of the ordered polypeptide in the process of destabilization, while in "cold denaturation" this gain is offset and exceeded overall by the loss in solvent entropy accompanying the interaction of the active solvent with the polypeptide backbone. Of course, we do not wish to imply here that the concomitant enthalpic changes are not of equivalent importance in the thermodynamic features of the transition.

It is entirely probable that such double transition will be found in other polypeptide-solvent systems. The helix-to-coil transition temperatures of polypeptides even with intrinsically very stable ordered conformations can be greatly depressed by the presence of a sufficiently strongly interacting solvent and, given a wide enough experimental temperature range, the lower transition might also be observable in many cases.

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Alkali Metal Catalyzed Polymerization of Some Conjugated Dienes Bearing an Allylic Proton

The alkali metal catalyzed polymerization of 1,3-pentadiene in tetrahydrofuran was found to be inhibited completely by triethylamine giving the dienyl alkali metal compound in place of poly(pentadiene). This observation led us to a general method for the preparation of pure dienyl alkali metal compounds:[1] *i.e.*, a conjugated or an unconjugated diene is allowed to react with an alkali metal in tetrahydrofuran in the presence of triethylamine. In this reaction, an unconjugated diene isomerizes to a conjugated one, and the latter reacts with an alkali metal, without any gas evolution, to give the dienyl alkali metal by the abstraction of a hydrogen atom from the methyl or methylene group adjacent to the conjugated system, and by the formation of the reduced dimer(s) of the conjugated diene. This finding gave us further insight into the mechanism of the well-known alkali metal catalyzed polymerization of some conjugated dienes.[2] This paper describes the results obtained with 1,3-pentadiene and 2,3-dimethyl-1,3-butadiene.

cis- and *trans*-pentadiene (**1**), C_5H_8 (1.5 mol), was allowed to react with dispersed potassium (1.0 mol) in an argon atmosphere in a tetrahydrofuran (2.0 mol)-triethylamine (1.0 mol) mixture to give crystalline pentadienylpotassium tetrahydrofuranate (**2**), $C_5H_7K \cdot C_4H_8O$, and a mixture of three reduced dimers (**3**), $C_{10}H_{18}$, following the stoichiometry represented in eq 1.[1]

$$\underset{\mathbf{1}}{4CH_3{-}CH{=}CH{-}CH{=}CH_2} + 2K \xrightarrow[(C_2H_5)_3N]{C_4H_8O}$$

$$\underset{\mathbf{2}}{2[CH_2 \overset{\cdots}{-} CH \overset{\cdots}{-} CH \overset{\cdots}{-} CH \overset{\cdots}{-} CH_2]K \cdot C_4H_8O} + \underset{\mathbf{3}}{C_{10}H_{18}}$$

$$\Big\downarrow D_2O \qquad (1)$$

$$DH_2C{-}CH{=}CH{-}CH{=}CH_2 \ (90\%)$$

$$H_3C{-}CH{=}CH{-}CH{=}CHD \ (10\%)$$

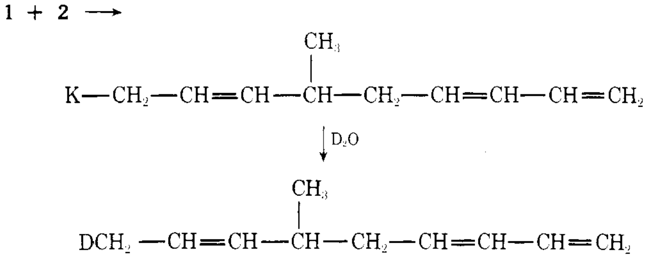
Table I
Polymerization of 1 and 5[a]

Monomer	Catalyst	Yield of Polymer (%)	Microstructure of Polymer 1,2 (%)	1,4 (%)	3,4 (%)
1	Metallic K	83	20	80	0
	2	82	25	75	0
5	Metallic K	85	35	65	
	5	85	34	66	

[a] Polymerization condition: catalyst, 1 mol % of monomer; solvent, H_4furan; temperature, 30°; time, 5 days for **1** and 4 days for **5**.

The crystalline dienylpotassium **2** behaved as a catalyst in the polymerization of **1** to give results quite similar to those obtained with a metallic potassium catalyst (Table I). Although this fact seems to suggest that the polymerization of **1** catalyzed by metallic potassium in the absence of amine proceeds *via* **2** as an initiation species, there is no evidence to rule out the possibility that the dimer dianion of potassium forms initially. The reaction between **1** and metallic potassium in which triethylamine was absent depends on a temperature; lower temperature favors the formation of **2** and higher one gives exclusively poly(pentadiene). In these cases, dipotassium dianion and reduced dimers could not be isolated in crystalline forms. These experimental results imply that triethylamine not only inhibits the polymerization of **1**, but also acts the transferrer of hydrogen to result in the formation of reduced dimers (**3**).

The information about the second step in the polymerization was obtained from the equimolar reaction of **2** with **1**, which was carried out in tetrahydrofuran at −35° for 2 hr. Deuteriolysis of this reaction mixture with D_2O gave 6-methyl-1,3,7-nonatriene-9-d_1 (**4**)[3] in 20% yield, in addition to poly(pentadiene). The yield of **4** was about 60% in the case of the corresponding crystalline dienylsodium. In contrast to this, the reaction carried out at 30° gave exclusively poly(pentadiene). These experimental results suggest that the second step of the polymerization is mainly the 1,4 addition of **1** to **2**, in good agreement with the microstructure of poly(pentadiene) (Table I), and that the polymerization proceeds *via* **2** with the monoanionic active species.



$$\mathbf{1} + \mathbf{2} \longrightarrow K{-}CH_2{-}CH{=}CH{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}CH{=}CH{-}CH{=}CH_2 \xrightarrow{D_2O} DCH_2{-}CH{=}CH{-}\overset{\overset{\displaystyle CH_3}{|}}{CH}{-}CH_2{-}CH{=}CH{-}CH{=}CH_2$$

4

2,3-Dimethyl-1,3-butadiene (**5**), C_6H_{10} (1.0 mol), was allowed to react with dispersed potassium (1.0 mol) in a tetrahydrofuran (2.0 mol)-triethylamine (1.0 mol) mixture in an argon atmosphere at 0° to give the dienylpotassium (**6**), $C_6H_8K_2 \cdot 2(C_4H_8O)$, as a yellowish powdery substance; yield, 60%. The filtrate contained the reduced dimer,

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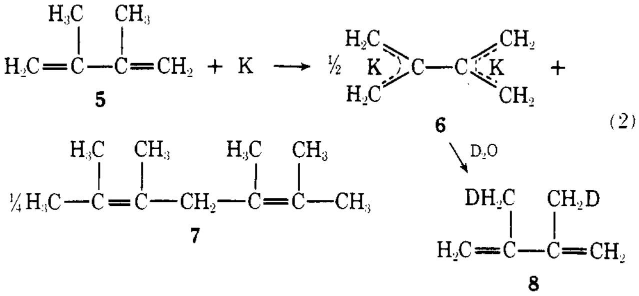
[1] H. Yasuda, T. Narita, and H. Tani, *Tetrahedron Lett.*, 2443 (1973).

[2] A. V. Tobolsky and C. E. Rogers, *J. Polym. Sci.*, **40**, 73 (1959); *ibid.*, **61**, 155 (1962).

[3] The structure of **4** is supported by following data: ir 1805, 1002, 896 (δ(CH) of terminal vinyl), 1655, 1601 (ν(C=C) of conjugated diene), 949 (δ(CH) of conjugated diene), 965 (δ(CH) of trans CH=CH); nmr δ 0.46 (d, 3 H, $CH_3{-}C{-}$) 1.08 (d, 2 H, $CH_2D{-}C{=}C$) 1.58 (t, 2 H, $={C}{-}CH_2{-}C{=}$) 4.65, 5.58 (m, 7 H, $CH_2{=}$, $-CH{=}CH-$); *Anal.* Calcd for $C_{10}H_{15}D$: 137. Found: 137 (mol wt by ms).

2,3,6,7-tetramethyl-2,6-octadiene (7),[4] $C_{12}H_{22}$; yield, 50%.



(2)

The nmr spectrum of 6 shows a single peak at δ 1.4 ppm and the deuteriolysis of 6 with D_2O gave 2,3-dimethylenebutane-*1,4-d*$_2$ (8)[5] in a quantitative yield. These results can be interpreted by assigning the symmetrical structure, which is represented in eq 2, for 6.

The polymerization of 5 was carried out in tetrahydrofuran at 30° with 6 or metallic potassium as a catalyst. Quite similar results were obtained with both catalysts (Table I). These results are also in good agreement with those reported by Schué.[6] Thus, the initiation reaction in the polymerization of 5 with metallic potassium is considered to be the formation of 6 and the polymerization proceeds *via* 6 with the dianionic active species.

(4) The structure of 7 is supported by following data: ir 1636 (ν(C=C)) 889 (trans δ(CH) of —CH=CH—); nmr δ 1.50 (s, 9 H, CH_3—) 1.98 (s, 2 H, —CH_2—C=); *Anal.* Found; 166 (mol wt by ms). Calcd for $C_{12}H_{22}$: 166.

(5) The structure of 8 is supported by the following data: δ 1.30 (s, 4 H, —CH_2D) 4.46 (s, 4 H, CH_2=); *Anal.* Found: 84 (mol wt by ms). Calcd for $C_6H_8D_2$: 84.

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Quasielastic Light Scattering from Nonideal Solutions

According to current quasielastic light-scattering theories on infinitely dilute solutions of macromolecules, internal relaxation modes can be observed for sufficiently large molecules.[1-4] These internal molecular relaxation terms, however, are coupled to the center-of-mass translational diffusion term. Therefore, the slowest relaxation time obtainable from light scattered by these macromolecules is predicted to be due to pure diffusion. Recent experimental results of quasielastic light scattering from solutions of DNA[5,6] and polyacrylamide[7] do not conform to this theoretical prediction. In these systems, two relaxation times differing by a factor of ~20–50 have the predicted K^2 dependence for translational diffusion. The presence of two modes of translational diffusion is assumed to be due to the highly nonideal nature of the solution in which molecular motions are strongly affected by neighboring molecules.

The subject of the present communication is the development of a general form for the autocorrelation function of the phototube current resulting from light scattered by nonideal solutions.[8] The phototube current autocorrelation function $\langle I(0)I(\tau)\rangle$ is related to the K-space polarizability of the sample $\alpha(\mathbf{K},\tau)$ by

$$\langle I(0)I(\tau)\rangle = A\langle\alpha^*(\mathbf{K},0)\alpha(\mathbf{K},0)\alpha^*(\mathbf{K},\tau)\alpha(\mathbf{K},\tau)\rangle \qquad (1)$$

where A is a proportionality constant, τ is the time delay, and the angular brackets denote the ensemble average. Restricting the development to center-of-mass motions, we write the excess polarizability of the scattering volume centered about the point defined by the vector $\mathbf{r}$ in an arbitrary reference frame as

$$\alpha(\mathbf{r},t) = \alpha\sum_J \delta[\mathbf{R}_J(t) - \mathbf{r}] \qquad (2)$$

where $\mathbf{R}_J(t)$ locates the center-of-mass of the Jth particle at time t and $\delta(x)$ is the Dirac delta function. All particles are assumed to have the same polarizability α.

The Fourier transform of eq 2 is the K-space polarizability

$$\alpha(\mathbf{K},t) = \alpha\sum_J \exp[-i\mathbf{K}\cdot\mathbf{R}_J(t)] \qquad (3)$$

Substitution of eq 3 into eq 1 gives the expression

$$\langle I(0)I(\tau)\rangle = A\alpha^4\sum_G\sum_H\sum_I\sum_J\langle\exp[-i\mathbf{K}\cdot(\mathbf{R}_G(0) - \mathbf{R}_H(0) + \mathbf{R}_I(\tau) - \mathbf{R}_J(\tau))]\rangle \qquad (4)$$

Since interference occurs only when quantities of opposite signs are paired, there are only four groups of time-dependent terms in eq 4; $G = J \neq H = I$, $G = I \neq J = H$, $G = J \neq H \neq I$, and $G \neq H \neq I \neq J$. That is, there are $N(N - 1)$ terms in the first two groups, $N(N - 1)(N - 2)$ terms in the third group, and $N(N - 1)(N - 2)(N - 3)$ terms in the fourth group. Thus, we define the time-dependent terms for the four groups by

$$C_1(\tau) \equiv \langle\exp[-i\mathbf{K}\cdot(\mathbf{R}_1(0) - \mathbf{R}_1(\tau))]\exp[-i\mathbf{K}\cdot(\mathbf{R}_2(\tau) - \mathbf{R}_2(0))]\rangle \qquad (5a)$$

$$C_2(\tau) \equiv \langle\exp[-i\mathbf{K}\cdot(\mathbf{R}_1(0) - \mathbf{R}_2(\tau))]\exp[-i\mathbf{K}\cdot(\mathbf{R}_1(\tau) - \mathbf{R}_2(0))]\rangle \qquad (5b)$$

$$C_3(\tau) \equiv \langle\exp[-i\vec{\mathbf{K}}\cdot(\mathbf{R}_1(0) - \mathbf{R}_1(\tau))]\exp[-i\mathbf{K}\cdot(\mathbf{R}_2(\tau) - \mathbf{R}_3(0))]\rangle \qquad (5c)$$

$$C_4(\tau) \equiv \langle\exp[-i\vec{\mathbf{K}}\cdot(\mathbf{R}_1(0) - \mathbf{R}_2(\tau))]\exp[-i\mathbf{K}\cdot(\mathbf{R}_3(\tau) - \mathbf{R}_4(0))]\rangle \qquad (5d)$$

where the subscripts 1, 2, 3, and 4 replace the alphabetic labels since the molecules are identical. The quantity $C_1(\tau)$ represents the correlation of two freely diffusing particles. In the infinite dilution case or Gaussian approximation, this term reduces to the square of the single particle correlation function

$$C_1(\tau) \longrightarrow D_1(\tau)D_1^*(\tau) \qquad \text{(infinite dilution)} \qquad (6)$$

where

$$D_1(\tau) \equiv \langle\exp[-i\mathbf{K}\cdot(\mathbf{R}_1(0) - \mathbf{R}_1(\tau))]\rangle \qquad (7)$$

and * denotes the complex conjugate. In more concentrated solutions or systems of very large particles, there may be a correlation between freely diffusing particles, such as an excluded volume effect. Therefore, $C_1(\tau)$ defined by eq

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