the modulus is in agreement with the previous, more limited results obtained on networks prepared from poly(*cis*-1,4-butadiene),[5,9] and from natural rubber.[12] The values of $2C_2$ reported in Table I are probably most reliable in the region of $f^*/(\alpha - \alpha^{-2}) \geq 1.0$ kg/cm^2; these results seem to suggest that the dependence of $2C_2$ on $v_{2,S}$ is strongest in the region $v_{2,S} < 0.5$. In contrast, the time required to reach mechanical equilibrium, while also decreasing with decreasing $v_{2,S}$ at constant values of the modulus, changes most markedly in the region of *large* $v_{2,S}$; a similar dependence is shown by the amount of stress relaxation occurring in a sample, as measured by the ratio of the equilibrium value of the stress to the initial value observed immediately upon sample elongation. Very importantly, at constant $v_{2,S}$, increase in degree of cross-linking seems in general to *increase* $2C_2$ but to *decrease* the nonequilibrium effects. These differences in behavior between $2C_2$ and the nonequilibrium characteristics would seem to support the previously reached conclusion[7] that, at least in the case of poly(dimethylsiloxane) networks, the $2C_2$ correction is not entirely due to nonequilibrium effects. Values of the sample rest lengths L_i obtained before and after the stress–elongation measurements were identical within experimental error and therefore such results, which have been used to characterize the permanent deformation of a sample,[5,9] are not included here. A final point of interest is the fact that only the networks prepared at the lowest polymer concentration ($v_{2,S} = 0.30$) ruptured in the elongation range α = 1.1–1.8, even though their moduli were very similar in magnitude to those of samples prepared at other, larger values of $v_{2,S}$. These additional results seem to support earlier contentions[5,9,12] that networks prepared by cross-linking a polymer in solution have very different topologies from those prepared in the bulk, undiluted state.

TABLE II
VALUES OF f_S^*/f_B^*

		Experimental		Theoretical	
$(v_{2,C})_S$	$v_{2,N}$	$\alpha = 1.3$	$\alpha = 1.7$	James, Guth	Flory
0.69	0.09	1.04	1.03	1.00	1.02
	0.12	1.05	1.03	1.00	1.03
0.58	0.09	1.07	1.06	1.00	1.04
	0.12	1.09	1.08	1.00	1.05
0.52	0.09	1.08	1.07	1.00	1.06
	0.12	1.12	1.13	1.00	1.07
0.45	0.09	1.09	1.08	1.00	1.08
	0.12	1.10	1.12	1.00	1.09
0.38	0.09	1.04	1.07	1.00	1.10
	0.12	1.05	1.09	1.00	1.13
0.28	0.09	1.03	1.07	1.00	1.17
	0.12	1.01	1.08	1.00	1.21

Acknowledgments. It is a pleasure to acknowledge the partial financial support provided by Grant No. 3151-A5 from the Petroleum Research Fund, administered by the American Chemical Society. R. M. J. also wishes to acknowledge, with gratitude, the postdoctoral fellowship provided by the Macromolecular Research Center of the University of Michigan.

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Vapor Sorption of *N,N*-Dimethylformamide on Poly(γ-benzyl α,L-glutamate)[1]

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ABSTRACT: Solvent activities for poly(γ-benzyl L-glutamate) solutions in *N,N'*-dimethylformamide have been determined at 25, 20, and 10° in the concentration range 70–100 vol % polymer. The results indicate that solvent activity is insensitive to temperature at constant composition in the concentration and temperature ranges studied. No evidence was found for the coexistence of two phases or for ordered side chains in the polypeptide. The results are compared with theories of solutions of rodlike molecules.

It is known that poly(γ-benzyl L-glutamate) (PBLG) dissolves in *N,N'*-dimethylformamide (DMF) in the form of the rodlike, α-helical conformation.[2] Only limited thermodynamic studies have been made on this system. At low polymer concentration the solutions are isotropic, while at higher concentrations they are anisotropic (liquid crystalline). Coexistence of isotropic and anisotropic phases is observed in an intermediate concentration range.[3] The temperature–composition phase diagram in the range −20 to 140° and 0–30 vol % polymer has been determined recently.[3] Solvent activities of dilute, isotropic solutions measured as a function of temperature and of solute molecular weight have been reported also.[4] In this paper we report the results of solvent activity measurements at 25, 20, and 10° and in the composition range 70–100 vol % polymer. The results are compared with the existing theories and with similar experimental work of Flory and Leonard.[5]

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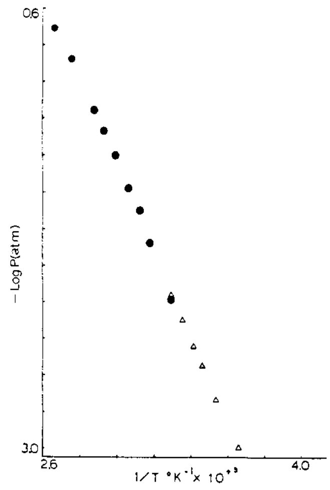

Figure 1. Vapor pressure of dimethylformamide as a function of temperature: (●) Ivanova and Geller,[6] (△) present work.

Experimental Section

PBLG (M_w = 310,000) was obtained from New England Nuclear. It was vacuum dried for more than 24 hr at 60° before use. DMF (Fisher Scientific Co., reagent grade) was vacuum distilled and dried before use. The vapor sorption apparatus was basically a quartz spring balance (Worden Quartz Products, Inc.) in a temperature-controlled environment located in an isolatable section of a vacuum-line. The quartz spring was calibrated with known weights and had a sensitivity of 1.6 mm/g. The weight increase due to sorption of solvent by PBLG was measured from the extension of the quartz spring by a cathetometer. A 12-cm o.d. tube which housed the suspension assembly was immersed in a constant-temperature bath. High-vacuum Teflon stopcocks were used to isolate the assembly and regulate the admission of solvent. The pressure of the system was measured by a Barocel electronic manometer (Datametrics, Inc.) calibrated with a McLeod gauge using dry air. The reading of the two pressure gauges agreed within 3%. The electronic manometer was checked further by measuring the temperature dependence of the vapor pressure of DMF. The results, shown in Figure 1, are seen to agree closely with and extend the work of Ivanova and Geller.[6] To obtain sorption equilibrium data solvent vapor was admitted into the evacuated (10^{-5} mm) balance and the system isolated. When no further weight increase was observed in the suspension assembly for at least 1 hr, equilibrium was assumed to have been obtained. The sorption equilibrium data were checked also by another method. After the solvent vapor was allowed into the vacuum chamber for at least an hour, the chamber was quickly evacuated, and again solvent was introduced into the chamber. The procedure of quick evacuation and subsequent introduction of solvent vapor into the vacuum chamber was repeated several times until at a certain fixed final pressure no further weight increase due to vapor sorption was detected. It was then assumed that equilibrium had been achieved. Agreement between the results obtained by the two methods assured that true equilibrium had been attained. We have also used the present apparatus to measure the solvent activities for the system PBLG–pyridine at 25° and have reproduced the results of Flory and Leonard.[5]

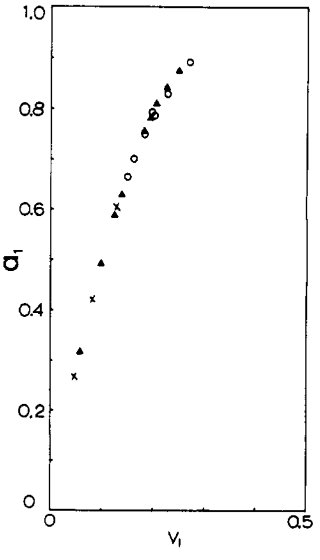

Figure 2. Vapor sorption at 25°: sample 2 (▲) ascending, (×) descending; sample 3 (○) ascending.

To compute the volume concentration, the polymer and solvent specific volumes were assumed to be concentration independent. The specific volume of PBLG was taken[5] as 0.787 cm^3 g^{-1} and assumed to be temperature independent. The specific gravity of DMF was taken as 0.945, 0.949, or 0.959 at 25, 20, or 10°, respectively.[7]

Results and Discussion

Solvent activities at 25, 20, and 10° are plotted as a function of solvent volume fraction in Figures 2–4. The PBLG samples used were in fibrous form. A sample weight of 103 (sample 1), 90.2 (sample 2), or 81.3 mg (sample 3) was used. The data were taken randomly by increasing (ascending) or decreasing (descending) solvent vapor pressures. The results obtained for the three different samples are seen to agree closely. Hysteresis, which was observed in the systems PBLG–pyridine and PBLG–ethylene dichloride with one of the two samples used by Flory and Leonard,[5] was not observed in the present work.

A PBLG film cast from DMF was used also for vapor sorption studies. The film, similar to form A of McKinnon and Tobolsky,[8] was prepared by making a 15% PBLG solution at 45° and vacuum evaporating the DMF at room temperature. The results obtained from the sample in film form indicated that solvent activities were about 10% higher than the values obtained from the study when the PBLG samples were in fibrous form. There is no reason to believe that the polymer film forms an anisotropic phase different from that formed with the fibrous polymer. We feel that the effect is more likely a kinetic one. An experiment with the PBLG–pyridine system showed that vapor sorption equilibrium with a fibrous sample was achieved in less than 5 hr, but took more than 20 hr for a sample in film form. The significant reduction in surface area upon making a film may present a large kinetic barrier such that diffusion to reach an equilibrium state may be more difficult to achieve. Consequently, the film data are thought to represent nonequilibrium data and are not shown.

Temperature variation of the solvent activity at fixed solution composition was not detected. This temperature invariance, a measure of the smallness of the partial molar heat of solution, is consistent with the partial molar heat obtained by direct calorimetric measurements at lower polymer composition (v_2 < 0.3).[9] Using the calorimetric heat, the calculated variation in solvent activity is less than 4% for a 15°

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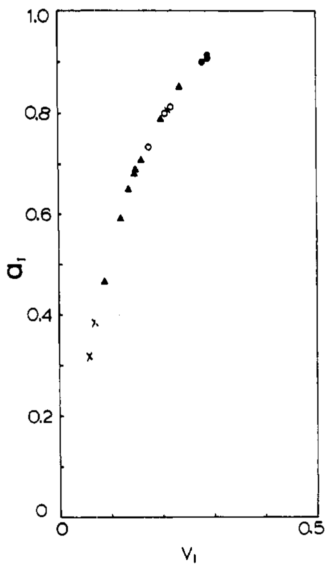

Figure 3. Vapor sorption at 20°: sample 1 (▲) ascending, (×) descending; sample 2 (○) ascending; sample 3 (●) ascending.

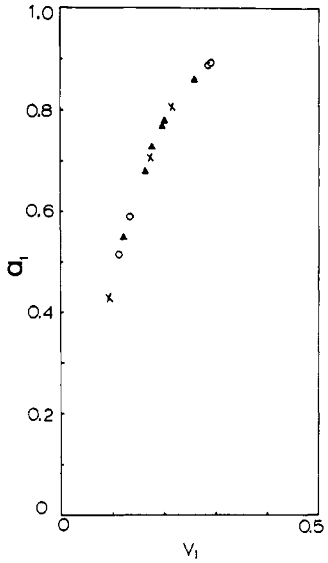

Figure 4. Vapor sorption at 10°: sample 2 (▲) ascending, (×) descending; sample 3 (○) ascending.

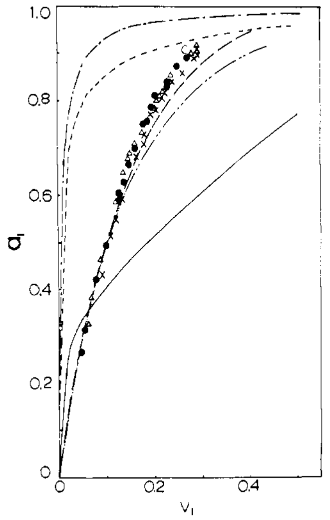

Figure 5. Comparison of experimental and theoretical isotherm. Experimental data from Figures 2–4 (— — —, - - - - -, and ———) based on Flory's impenetrable rod model with χ = 0, −0.1, and −1.0, respectively; (– – –) Flory–Leonard model with side-chain mixing; (— – —) Wee equation (6) with χ = 0, m = 0.1, and c = 1.5.

change in temperature, an effect comparable to the experimental precision. We thus conclude that at high polymer composition the solvent partial molar heat of solution is not substantially larger than in the formation of more dilute polymer solution.

In the system studied, isotropic–anisotropic or anisotropic–anisotropic phase equilibria occur at certain temperatures and compositions.[3] The existence of such biphasic regions would show here as a region of constant solvent activity. As all measured solvent activities were monotonic functions of solvent composition, no phase boundaries occur in the 70–100 vol % polymer region in the temperature range studied.

Theories of solutions of rodlike particles have been limited either to very dilute athermal solutions[10,11] or to the approximate approach of lattice theory.[12–14] In Flory's theory of solutions of impenetrable, rodlike particles, the activity a_1 of solvent in the anisotropic phase is given by

$$a_1 = v_1 \exp\{[(y - 1)/x]v_2 + 2/y + \chi v_2^2\} \qquad (1)$$

where v_1 and v_2 are respectively the volume fractions of solvent and solute, x is the polymer axial ratio, χ is the thermodynamic interaction parameter, and y is a disorientation parameter. At high polymer concentration, where the rods are perfectly ordered, y is equal to unity. At lower concentrations, it is given by the solution of the equation

$$v_2 = [x/(x - y)][1 - \exp(-2/y)] \qquad (2)$$

At high concentrations, where $y = 1$ and perfect alignment of long rods prevails at equilibrium, a_1 is given by the expression for a solution with ideal entropy of mixing

$$a_1 = x_1 \exp(\chi v_2^2) \qquad (3)$$

where x_1 is the mole fraction of solvent. In Figure 5, a_1 *vs.* v_1 calculated from eq 1, 2, and 3 for χ values of −1.0, −0.1, and 0 is plotted. From the general features of the curves, it is clear that the discrepancy between the predicted values and experimental data cannot be removed by adjusting the value of χ. It has been found that in dilute, isotropic solutions of PBLG in DMF, χ is approximately equal to 0.5 at 22°.[4] Small values of χ, *i.e.*, $\chi \approx 0$ at 22°, have been reported also.[3] Using either value of χ would make the discrepancy between the theory and present experimental data even greater.

Flory and Leonard[5] obtained similar results for the systems PBLG–pyridine, PBLG–dichloroethane, and poly(β-benzyl L-aspartate)–chloroform at 25° and in the concentration range 60–100 vol % polymer. They found that their data could not be fitted with values calculated from Flory's theory for solutions of impenetrable rods. To account for this discrepancy, they considered the mixing of solvent with flexible, disoriented polymer side chains. Assuming that mixing of solvent with randomly oriented side chains dominates the concentrated

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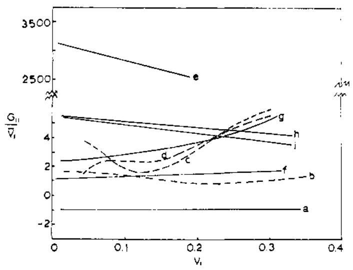

Figure 6. Cluster function ($G_{11}/\bar{v}_1$) as a function of v_1: (a) ideal solution, equal size molecules; (b) benzene–rubber;[18] (c) DMF–PBLG, 25°; (d) DMF–PBLG, 10, 20, and 25° data combined; (e) rigid, impenetrable, athermal rods (eq 10); (f) Flory–Leonard model (eq 12), $\chi = 0$; (g) Flory–Leonard model, $\chi = 0.45$; (h) Wee model (eq 15), side chains attached; (i) Wee model, side chains unattached.

solution thermodynamic behavior for these systems, eq 4 was used to correlate their data

$$a_1 = v_1' \exp(v_2' + \chi(v_2')^2) \tag{4}$$

where v_1' is the volume fraction of solvent calculated on the basis of mixing being confined to the side chains. The relationship of v_1' and v_2' to v_1 and v_2 is given by

$$v_2'/v_1' = (M_s/M_u)(v_2/v_1) \tag{5}$$

where M_s and M_u are respectively the molecular weights of the side chain and of the entire peptide unit. The data of Flory and Leonard were found to fit eq 4 reasonably if χ values of 0.35 and 0.2 were assumed for PBLG in pyridine and dichloroethane, respectively, and a value of zero was assumed for poly(β-benzyl L-aspartate) in chloroform. In Figure 5, solvent activity a_1 *vs.* v_1 calculated from eq 4 and 5 for $\chi = 0.6$ is shown. Reasonable agreement is found between the predicted values and the experimental data.

In deriving eq 4 and 5, it has been assumed that the side chains of the polymer in solution are disordered and the mixing of solvent occurs exclusively within the side-chain domain.[5] If the side chains of PBLG in DMF are ordered, as proposed by Parry and Elliott,[15] to account for their X-ray diffraction data, a sigmoidal shape in the a_1 *vs.* v_1 curve near $v_1 = 0$ should be observed.[5] Since such behavior is apparently absent in the present results, we conclude that the side chains of PBLG in DMF in the region 70–100% polymer are disordered.

Modification of Flory's lattice theory to allow for side chains and main-chain flexibility has been made.[16] In this model, disordered side chains are assumed to be either attached to or cut off from the main-chain backbone. For the former case, a_1 for the anisotropic phase is given by

$$a_1 = v_1 \exp\left[\frac{v_2}{x(1 + mc)}(y - 1) + \frac{2}{y} + \frac{v_2 mc}{1 + mc} + \chi \frac{mc}{1 + mc} v_2^2\right] \tag{6}$$

and for the latter case by

$$a_1 = v_1 \exp\left[\frac{v_2(c - 1)m}{1 + mc} + \frac{v_2}{1 + mc}\left(\frac{y - 1}{x}\right) + \frac{2}{y} + \chi \frac{mc}{1 + mc} v_2^2\right] \tag{7}$$

where m is related to the number of side chains per main-chain cell, c is related to the number of flexible units per side chain, x is the axial ratio of the main chain, χ is the thermodynamic interaction parameter, and y is the equilibrium index of orientation. The value of y (>1) is given by the solution of

$$v_2 = (1 + mc)(1 - e^{-2/y})/[1 - (y/x)] \tag{8}$$

Activities calculated from eq 6–8 are reasonably insensitive to χ and x at fixed c and m. If c and m are taken as adjustable parameters, numerous combinations will give a reasonable fit to the experimental data. Shown in Figure 5 is a curve calculated from eq 6 and 8 with $\chi = 0$, $x = 150$, $c = 1.5$, and $m = 0.1$.

An alternative and perhaps more informative way to compare theory with experiment is through the use of the Zimm–Lundberg cluster function ($G_{11}/\bar{v}_1$),[17,18] which for a two-component system is given by

$$G_{11}/\bar{v}_1 = -v_2[\partial(a_1/v_1)/\partial a_1]_{P,T} - 1 \tag{9}$$

where $\bar{v}_1$ is the partial molar volume of component 1. An additional term belonging to eq 9 involving the isothermal compressibility has been dropped, as it is small in condensed systems. The cluster function is defined such that $v_1G_{11}/\bar{v}_1$ is the mean number of type 1 molecules in excess of the mean concentration of type 1 molecules in the neighborhood of a given type 1 molecule. For an athermal binary solution of equal size molecules the cluster function is independent of concentration and equal to -1 (Figure 6a). For nearly athermal solutions of flexible polymers, the cluster function is sensibly independent of concentration (Figure 6b) and in good agreement with the theoretical lattic model value of $z/(z - 2)$, if the lattice coordination number z is taken as 4.[18]

The a_1/v_1 values of the data presented herein were fitted to a power series in activity by a least-squares fit. The cluster function was determined according to eq 9 and shown in Figure 6c,d. At small v_1, the PBLG–DMF values lie close to the value for flexible chain polymers but increase at higher solvent concentrations. At the lowest solvent activities there is considerable uncertainty in the $G_{11}/\bar{v}_1$ values determined from the experimental data. These values can be compared to those appropriate to the various models. For aligned, impenetrable, athermal rods, the clustering function can be determined from eq 3 and 9. It is given by

$$G_{11}/\bar{v}_1 = (a - 1)v_2 - 1 \tag{10}$$

where

$$a = \rho_1 M_2/\rho_2 M_1 \tag{11}$$

Here ρ is the density and M is the molecular weight. Values determined from eq 10 are shown in Figure 6e and should be appropriate, according to eq 2, for solvent volume fractions less than 0.15. The large discrepancy is a further illustration of the deviation of the PBLG–DMF system from impenetrable, rigid-rod behavior. The cluster function for the empirical Flory–Leonard model is

$$G_{11}/\bar{v}_1 = -[(v_2/v_1)(1 - A - B)/(1 - A - B + v_2/v_1)] - 1 \tag{12}$$

where

$$A = M\mu(M_sv_2 + M\mu)/M_sv_2 + M\mu v_1)^2 \tag{13}$$

and

$$B = 2\chi M\mu/[M_sv_2(1 + M\mu v_1/M_sv_2)^3] \tag{14}$$

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The cluster function given by eq 12 is shown in Figure 6f for an athermal solution and in Figure 6g for a system with χ = 0.45. The cluster function determined from eq 6 is given by

$$G_{11}/\bar{v}_1 = -[(v_2/v_1)(C - D)/(C - D - v_2/v_1)] - 1 \quad (15)$$

where

$$C = mcv_2\left[1 + \frac{(y-1)}{xmc} + 2\chi v_2\right]\Big/(1 + mc) \quad (16)$$

and

$$D = [2x(1 + mc) - y^2v_2]/ \\ \left[1 + \frac{y^2}{2(x-y)} - \frac{(1+mc)x}{(x-y)v_2}\right](1 + mc)2x \quad (17)$$

The cluster function derived from eq 7 differs from eq 16 only in the additional term of eq 16, $mv_2/(1 + mc)$. Calculated curves based on these equations are shown in Figure 6i.

The Flory-Leonard equation with χ = 0.45 gives computer curves in good agreement with the experimental data, whereas χ = 0.6 gave a better fit to the $a_1 - v_1$ data (Figure 5). The Wee equations, derived to determine the effect of flexible side chains on phase equilibria, do not fit as well. This is not surprising, as the rodlike character of the main chain still plays a significant role in the activity expression at low concentration, in contrast to the Flory-Leonard expression.

It is clear from the comparison of the experimental data with various theories that the free energy associated with the initial solution process is controlled by polymer side chain–solvent mixing. This is in marked contrast to more dilute polymer solutions, where the rodlike behavior of the molecules is of major importance to the thermodynamics of this system.[3,12]

Catenation and Kinetics of the Diels–Alder Step-Growth Reaction in the Synthesis of Phenylated Polyphenylenes[1]

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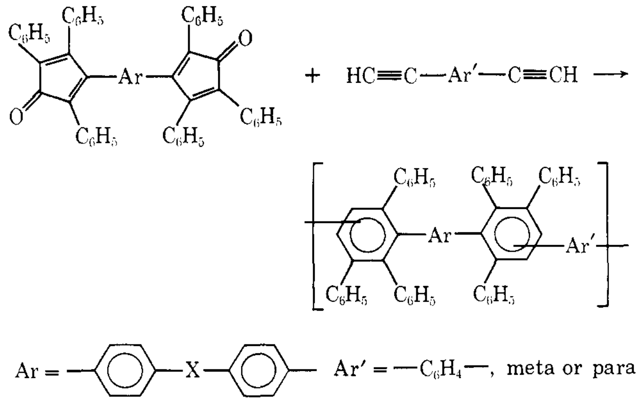
ABSTRACT: The Diels–Alder step-growth polymerization of biscyclopentadienones with bisacetylenes, which can produce either para or meta catenation in the benzene ring formed from the reaction, was shown by a model reaction to yield both types of catenation. The model reaction of 3-(4-biphenylyl)-2,4,5-triphenylcyclopentadienone with 4-ethynylbiphenyl gave products in which the ratios (para to meta) varied with the reaction temperature from 0.55 at 100° to 1.0 at 255°. The application of the Arrhenius law to the data yields a difference in the enthalpy of activation of ($\Delta H_m^{\ddagger} - \Delta H_p^{\ddagger}$) of -1.6 kcal/mol and a difference in the entropy of activation ($\Delta S_m^{\ddagger} - \Delta S_p^{\ddagger}$) of 3.0 eu. The polymerization reaction of 3,3′-(oxydi-*p*-phenylene)bis(2,4,5-triphenylcyclopentadienone) followed a second-order rate law, and the rate constants at the temperatures of 225, 200, and 175° were found to be 1.14×10^{-3}, 4.6×10^{-4}, and 2.6×10^{-4} l./(mol sec), respectively. The Arrhenius activation parameters as calculated from the rate constants were $\Delta H^{\ddagger} = 12.4$ kcal/mol and $\Delta S^{\ddagger} = -48$ eu, consistent with a Diels–Alder reaction which requires a low ΔH and a large negative ΔS.

The Diels–Alder reaction, or diene synthesis, has long been utilized in synthetic organic chemistry, and in many instances high yields of the adduct are obtained. The Diels–Alder reaction has been employed as a step-growth reaction in the formation of linear, ladder, and stepladder polymers.[2,3] Polymer formation is particularly effective when a small molecule such as carbon monoxide, carbon dioxide, or sulfur dioxide is lost during the reaction, and thus high yields of polymer can be obtained.

High molecular weight polymers containing the polyphenylene units have been successfully synthesized by the utilization of the Diels–Alder reaction of bistetracyclones and bisethynylbenzenes.[4-10] During the step-growth reaction of this poly-



X = nil, O, S, $(CH_2)_n$
n = 3, 4, 5, 10, 14

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