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Estimation of Solubility Parameters for Some Olefin Polymers and Copolymers by Inverse Gas Chromatography

K. Ito[1] and J. E. Guillet*

Department of Chemistry, University of Toronto, Toronto, Canada M5S 1A1.

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ABSTRACT: Flory–Huggins χ parameters have been determined by gas chromatography at 30 °C for ten standard hydrocarbons in ethylene (40%)–propylene (60%) copolymer, *cis*-polyisoprene, and amorphous polypropylene to estimate the polymer solubility parameter (δ_2^∞) by the method developed by DiPaola-Baranyi and Guillet. The results are as follows: $\delta_2^\infty = 7.70 \pm 0.11$ for ethylene–propylene, 7.96 ± 0.10 for *cis*-polyisoprene, and 7.67 ± 0.16 for polypropylene. The parameters for ethylene–propylene were also estimated by extrapolation from the higher temperature data (63–83 °C) and found to be in good agreement with those estimated directly.

The solubility parameter concept has been used extensively in practical applications of polymers. DiPaola-Baranyi and Guillet[2] have recently shown that inverse gas chromatography, using a polymer as the stationary phase, can be a simple and convenient method for estimating solubility parameters for polymers. The method is based on the principle that the Flory–Huggins χ parameter can be readily determined from retention data on various small molecule probes and that χ can be related to solubility parameters by Hildebrand–Scatchard theory[4] combined with Flory theory,[5] as follows:

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 \tag{1}$$

where χ has free-energy characteristics, i.e.,

$$\chi = \chi_H + \chi_S \tag{2}$$

and V_1 is the molar volume of the probe used, δ_1 is the solubility parameter of the probe, and δ_2 is the solubility parameter of the polymer. In the usual experiment, χ is determined under conditions approximating infinite dilution of the probe in the polymer, and hence the value of δ_2 is more correctly designated δ_2^∞, since it is also an infinite dilution quantity. For reasons outlined previously,[2] this quantity may have more fundamental significance than the value of δ_2 measured at finite solute concentrations by classical methods such as swelling or solubility measurements. Furthermore, at the high dilution of the experiment, it is possible that the assumptions of regular solution behavior, inherent in the Hildebrand–Scatchard treatment, are more closely fulfilled.

The method has been successfully applied to estimate consistent δ_2^∞ values for polystyrene at 193 °C, poly(methyl acrylate) at 100 °C, and poly(vinyl acetate) at 135 °C, using a variety of standard hydrocarbon solutes of different δ_1 values. δ_2^∞ was also estimated at 25 °C, using χ parameters computed by extrapolation of the higher temperature data according to

$$\chi = \alpha + \beta/T \tag{3}$$

where the constants α and β should have characteristics of entropy and enthalpy, respectively. This empirical equation is usually valid only for relatively small ranges of temperature; however, the δ_2^∞ values thus obtained were shown to agree well with literature data, supporting the idea that the derived parameters might be practically useful in predicting polymer solubility even at finite concentrations.

The present work extends the method to polymers including ethylene–propylene copolymer (EPR), *cis*-polyisoprene (PIP), and amorphous polypropylene (PP). Since these polymers have very low glass-transition temperatures (−20 °C or lower), the GLC data can be obtained close to room temperature, so that their δ_2^∞ values can be determined directly and compared with those estimated by the extrapolation method. It will also be shown that the χ parameters are more properly expressed by the relation derived by Huggins[7] and by Scott and Magat:[8]

$$\chi = (V_1/RT)(\delta_1 - \delta_2)^2 + \gamma \tag{4}$$

where γ is an entropy correction term which is often considered to be a constant near 0.3 for many polymers.[8,9]

Experimental Section

Ethylene–propylene rubber was Exxon Vistalon 404 with a composition of 40% ethylene and 60% propylene. *cis*-Poly-

Table I
Column Parameters

polymer	coating solvent	loading, %[a]	polymer mass, g	length, in.	o.d., in.
	packing and column				
ethylene-propylene rubber	xylene	8.34	0.412	18	1/4
			0.0313	12	1/8
cis-polyisoprene	benzene	8.25	0.329	18	1/4
			0.0826	4	1/4
polypropylene	benzene	7.29	0.373	18	1/4
			0.0826	12	1/8

[a] Inert support was Chromosorb G, AW, DMCS, 70-80 mesh.

Table II
Thermodynamic Parameters of Hydrocarbons in Ethylene-Propylene Rubber at 73 °C

solute	V_1, cm^3/mol	ΔH_v, kcal/mol[a] obsd	calcd	δ_1	$(a_1/w_1)^\infty$ [b]	ΔH_1^∞,[c] kcal/mol	χ
2,2,4-trimethylpentane	176.2	7.81 ± 0.04	7.78	6.36	4.9	0.31 ± 0.02	0.33
n-hexane	141.4	6.99 ± 0.18	6.83	6.68	5.5	0.25 ± 0.09	0.38
n-octane	173.4	9.20 ± 0.04	9.10	7.01	4.7	0.33 ± 0.03	0.30
n-decane	206.3	11.41 ± 0.07	11.49	7.21	4.4	0.24 ± 0.05	0.28
cyclohexane	115.6	7.36 ± 0.08	7.29	7.60	3.9	0.22 ± 0.05	0.22
tert-butylbenzene	163.0	10.79 ± 0.07	10.81	7.87	3.7	0.46 ± 0.04	0.27
ethylbenzene	129.5	9.47 ± 0.03	9.43	8.24	3.8	0.51 ± 0.02	0.31
benzene	95.1	7.53 ± 0.02	7.45	8.49	4.3	0.57 ± 0.02	0.44

[a] The error limits quoted are variances (1σ) based on least-squares analysis of the data. [b] $\ln (a_1/w_1)^\infty = \ln (273.16R/p_1{}^0 V_g M_1) - p_1{}^0(B_{11} - V_1)/RT$. [c] $\Delta H_1{}^\infty = R\ \partial \ln (a_1/w_1)^\infty/\partial(1/T)$.

Table III
Temperature Dependence of the χ Parameter of Hydrocarbons in Ethylene-Propylene Rubber

solute	intercept α	slope β	correl coeff	χ at 30 °C calcd[a]	obsd
2,2,4-trimethylpentane	−0.413	256	0.9982	0.43	0.42
n-hexane	−0.389	266	0.9350	0.49	0.46
n-octane	−0.466	266	0.9950	0.41	0.42
n-decane	−0.299	203	0.9726	0.37	0.34
cyclohexane	−0.418	222	0.9754	0.31	0.33
tert-butylbenzene	−0.577	295	0.9899	0.39	0.37
ethylbenzene	−0.670	338	0.9988	0.45	0.45
benzene	−0.703	394	0.9996	0.60	0.60

[a] $\chi = \alpha + \beta/T$

isoprene ($\bar{M}_n$ 126 000) was obtained from Polysar, and amorphous polypropylene was obtained from Eastman (Epolene D-10). These polymers were completely soluble in the solvents indicated in Table I and were used as supplied. Column preparations and collection of retention data were carried out as before.[2,3] Two columns of different size containing low and high polymer loadings were prepared for each polymer (see Table I) and used with ten solutes, including 2-methylbutane (bp 28 °C) and *tert*-butylbenzene (bp 169 °C), within an accessible range of retention time from 1 to 40 min at a flow rate of 30 mL/min. The retention volume was confirmed to be independent of solute sample size in all cases studied, and reproducibility was good (within ±5%) between columns with different loadings.

Data reduction was followed as described in previous publications.[2,3] The following relations were used to obtain the specific retention volume V_g (corrected to 0 °C) and the χ parameter:

$$V_g = \left(\frac{t_R F}{w}\right)\left(\frac{273.16}{T_r}\right)\left(\frac{P_o - P_w}{P_o}\right)\left(\frac{3}{2}\right)\left(\frac{(P_i/P_o)^2 - 1}{(P_i/P_o)^3 - 1}\right) \quad (5)$$

$$\chi = \ln\left(\frac{273.16Rv_2}{p_1{}^0 V_g V_1}\right) - 1 - p_1{}^0(B_{11} - V_1)/RT \quad (6)$$

where t_R is the net retention time, F is the flow rate measured with a soap bubble flow meter at ambient temperature T_r (K), w is the mass of polymer in the column, P_i and P_o are the column inlet and outlet pressure, and P_w is the water vapor pressure at T_r. The solute (probe) parameters, including the vapor pressure ($p_1{}^0$), second virial coefficient (B_{11}), and the molar volume (V_1), were obtained or computed from literature sources[10] as before.[2,3] The polymer specific volumes (v_2) for EPR,[11] PIP,[12] and PP[13] were computed from literature data.

Results and Discussion

Various thermodynamic parameters, including weight fraction activity coefficient $(a_1/w_1)^\infty$, partial molar heat of mixing $\Delta H_1{}^\infty$ at infinite dilution, and the Flory–Huggins parameter χ, were first determined for eight hydrocarbons in EPR by measuring the retention volumes over the temperature range 63–83 °C. Table II summarizes these data at the midpoint, 73 °C. The values of $(a_1/w_1)^\infty$, $\Delta \bar{H}_1{}^\infty$, and χ are all of the magnitude expected for the polymer–solvent case. They appear to have their minimum (corresponding to the largest solubility) around the solutes *n*-octane ($\delta_1 = 7.01$), *n*-decane ($\delta_1 = 7.21$), or cyclohexane ($\delta_1 = 7.60$). The polymer solubility parameter δ_2 for EPR was then evaluated from the relation derived from eq 1:

$$\frac{\delta_1{}^2}{RT} - \frac{\chi}{V_1} = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \frac{\delta_2{}^2}{RT} \quad (7)$$

The plot of $(\delta_1{}^2/RT) - (\chi/V_1)$ against δ is shown in Figure 1a. The linear correlation is excellent, and a least-squares analysis gave $\delta_2 = 7.18 \pm 0.11$ and 7.26 ± 0.12 from the slope and the intercept, respectively, at 73 °C.

Table IV

V_1, δ_1, and χ Values for Hydrocarbons in Ethylene-Propylene Rubber, *cis*-Polyisoprene, and Polypropylene at 30 °C

			χ					
			EPR		PIP		PP	
solute	V_1	δ_1	obsd	calcd[a]	obsd	calcd[b]	obsd	calcd[c]
2-methylbutane	118.4	6.63	0.59	0.56	0.57	0.62	0.91	0.68
2,2,4-trimethylpentane	167.1	6.83	0.42	0.48	0.46	0.62	0.58	0.67
n-pentane	117.0	6.95	0.52	0.44	0.52	0.47	0.64	0.57
n-hexane	132.5	7.20	0.46	0.39	0.50	0.40	0.48	0.57
n-octane	164.5	7.49	0.42	0.34	0.46	0.33	0.55	0.48
n-decane	196.9	7.67	0.34	0.33	0.43	0.30	0.29	0.47
cyclohexane	109.4	8.15	0.33	0.37	0.29	0.28	0.44	0.51
tert-butylbenzene	156.4	8.29	0.38	0.42	0.22	0.30	0.61	0.57
ethylbenzene	123.7	8.74	0.45	0.55	0.29	0.40	0.72	0.71
benzene	90.0	9.08	0.60	0.61	0.41	0.46	0.74	0.77

[a] Equation 4; $\delta_2 = 7.70$, $\gamma = 0.33$. [b] Equation 4; $\delta_2 = 7.96$, $\gamma = 0.27$. [c] Equation 4; $\delta_2 = 7.67$, $\gamma = 0.47$.

Table V

Estimation of δ_2 and γ Parameters for Ethylene-Propylene Rubber, *cis*-Polyisoprene, and Polypropylene

	δ_2 from eq 7		γ/V_1 from intercept	γ from	
system	slope	intercept	of eq 9[a]	eq 11[b]	eq 4[c]
EPR, 73 °C	7.18 ± 0.11	7.26 ± 0.12	0.0016	0.24	0.21 ± 0.07
EPR, 30 °C	7.70 ± 0.11	7.80 ± 0.10	0.0026	0.35	0.33 ± 0.07
PIP, 30 °C	7.96 ± 0.10	8.03 ± 0.09	0.0019	0.26	0.27 ± 0.10
PP, 30 °C	7.67 ± 0.16	7.81 ± 0.16	0.0035	0.48	0.47 ± 0.11

[a] $\gamma/V_1 = |-\text{intercept}|$ of $(\delta_1^2/RT - \chi/V_1)$ vs. δ_1 plot $- \delta_2^2/RT$. [b] $\gamma = [\gamma/V_1]_{\text{above}} V_{1(\text{av})}$, where $V_{1(\text{av})}$ is the average of V_1 of the solutes used. [c] Average with standard error for $\gamma = \chi_{\text{obsd}} - (V_1/RT)(\delta_1 - \delta_2)^2$.

The χ values obtained over the temperature range 63–83 °C were analyzed according to eq 3 to estimate the constants α and β. The results are given in Table III, where the corresponding correlation coefficient shows, in general, a good linear correlation between χ and $1/T$. The values of α and β so determined were then used to calculate χ values at 30 °C by extrapolation. Table III includes these χ values as well as those determined directly from experiments at 30 °C. The agreement is quite good, which lends support to the method used previously to calculate χ and δ values at 30 °C from data obtained at higher temperatures.[1]

Since the molar volume V_1 and the latent heat of vaporization ΔH_v of the standard hydrocarbon solutes is readily available or may be computed from the literature,[10] the solubility parameter δ_1 of the solute probe can also be easily estimated at any desired temperature from the definition

$$\delta_1 = [(\Delta H_v - RT)/V_1]^{1/2} \tag{8}$$

ΔH_v, the heat of vaporization of the probe molecule, can be obtained directly from chromatographic data from the relation

$$\Delta H_v = \Delta \bar{H}_1^{\infty} - \Delta H_s \tag{9}$$

where ΔH_s is the experimental heat of solution and $\Delta \bar{H}_1^{\infty}$ is the partial molar heat of mixing. These quantities are determined from the variation of the retention volume and the activity coefficient, respectively, with temperature.[1] ΔH_v can also be computed from the relation

$$\Delta H_v = \text{MW}(d - et) \tag{10}$$

where t is the temperature in °C and d and e are constants given in ref 9. Table II includes, for comparison, the ΔH_v values calculated from eq 10, which show very good agreement with those determined from the retention data.

Figure 1b shows the linear plots of $(\delta_1^2/RT) - (\chi/V_1)$ against δ_1, using the χ values extrapolated to 30 °C. The line is indistinguishable from the extrapolated values shown in Figure 1a, and the derived δ_2 values by least-squares analysis with eq 7 are 7.61 ± 0.11 and 7.69 ± 0.12 from the slope and the intercept, respectively. The corresponding values, using the χ data observed directly (Figure 1c), are 7.70 ± 0.11 and 7.80 ± 0.10, in good agreement with the above, again supporting the previous extrapolation procedure for estimating δ_2 at room temperature.

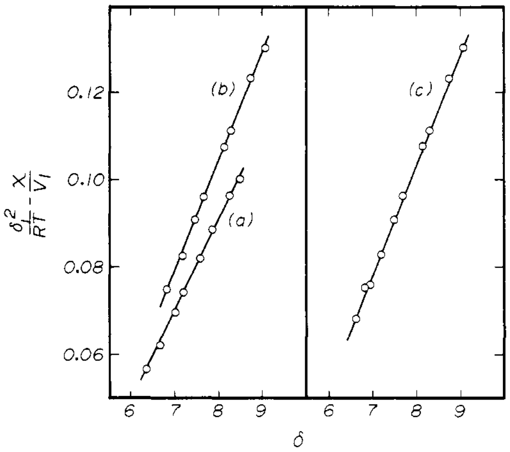

Figure 1. Estimation of solubility parameter for ethylene–propylene rubbers: (a) 73 °C, δ_2(slope) = 7.18 ± 0.11, δ_2(intercept) = 7.26 ± 0.12; (b) extrapolation to 25 °C, δ_2(slope) = 7.61 ± 0.11, δ_2(intercept) = 7.69 ± 0.12; (c) direct measurement at 30 °C, δ_2(slope) = 7.70 ± 0.11, δ_2(intercept) = 7.80 ± 0.10.

Table IV summarizes the χ values determined at 30 °C for ten hydrocarbon solutes in EPR, PIP, and PP together with the V_1 and δ_1 values. χ values in all systems are smaller than unity, as expected for polymer–solvent systems. It appears from comparison of the χ values that the hydrocarbons in general are slightly less soluble in PP than in PIP or EPR and that PIP tends to dissolve aromatic probes more readily than EPR and PP.

Plots of $(\delta_1^2/RT) - (\chi/V_1)$ against δ_1 are shown in Figures 1c and 2, and the δ_2 values determined by a least-

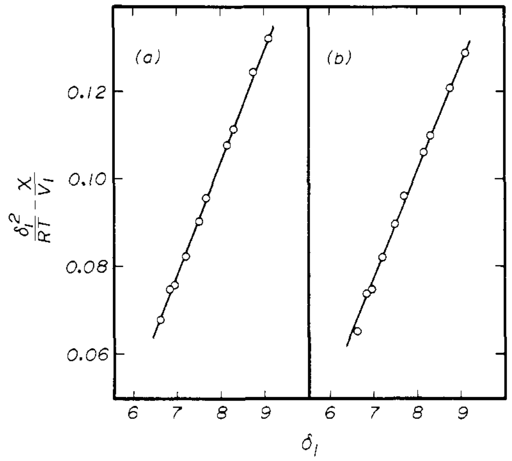

Figure 2. Estimation of solubility parameter for: (a) *cis*-polyisoprene at 30 °C, δ_2(slope) = 7.96 ± 0.10, δ_2(intercept) = 8.03 ± 0.09; (b) polypropylene at 30 °C, δ_2(slope) = 7.67 ± 0.16, δ_2(intercept) = 7.81 ± 0.16.

Table VI
χ Parameters for Hydrocarbons in Ethylene-Propylene Rubber at 30 °C

solute	χ_{obsd}	χ_{calcd} from eq 1[a]	γ (= $\chi - \chi_{\text{calcd}}$)	χ_{calcd} from eq 4[c]
2-methylbutane	0.59	0.23	0.36	0.56
2,2,4-trimethylpentane	0.42	0.21	0.21	0.48
n-pentane	0.52	0.11	0.41	0.44
n-hexane	0.46	0.06	0.40	0.39
n-octane	0.42	0.01	0.41	0.34
n-decane	0.34	0.00	0.34	0.33
cyclohexane	0.33	0.04	0.29	0.37
tert-butylbenzene	0.37	0.09	0.29	0.42
ethylbenzene	0.45	0.22	0.23	0.55
benzene	0.60	0.28	0.32	0.61

[a] With δ_2 = 7.70. [b] $\gamma = \chi_{\text{obsd}} - (V_1/RT)(\delta_1 - \delta_2)^2$. [c] With δ_2 = 7.70 and γ = 0.33.

squares analysis are summarized in Table V. It should be noted that, in applying eq 7, the δ_2 values derived from the intercept were slightly but consistently higher than those from the slope and moreover that in spite of the excellent linearity of the plots in Figures 1 and 2, the χ values recalculated from eq 1, using δ_2 calculated from the slope, were always significantly lower than those observed, as exemplified in Table VI for EPR, 30 °C system. In order to resolve this discrepancy, eq 4 derived by Huggins[7] and by Scott and Magat[8] was used in place of eq 1. This can be rewritten as

$$\frac{\delta_1^2}{RT} - \frac{\chi}{V_1} = \left(\frac{2\delta_2}{RT}\right)\delta_1 - \left(\frac{\delta_2^2}{RT} + \frac{\gamma}{V_1}\right) \tag{11}$$

Therefore, the plot of $(\delta_1^2/RT) - (\chi/V_1)$ against δ_1 should also give $2\delta_2/RT$ as the slope but give $(\delta_2^2/RT) + (\gamma/V_1)$ instead of δ_2^2/RT as the intercept. Fortunately, the contribution of the term γ/V_1 to the intercept may be estimated to be only 3% or less,[9] so that in this type of plot very similar values of δ_2 can be obtained both from the slope and the intercept, although those from the slope should be taken as more correct. In fact, in all of the present systems (Table V), the estimated value of γ/V_1 from the observed intercept was found to be in the range from 0.0016 to 0.0035, which corresponds to only 2 to 3% error in the intercept. Although the contribution of γ/V_1 in the plots according to eq 11 can be relatively small, the values of γ, estimated from these γ/V_1 values, are in a range of 0.24 to 0.48 (Table V), which will make an important contribution to the predicted value of χ parameters, particularly when χ is small, as in the present case.

For example, Table VI summarizes the experimental χ parameters obtained for various hydrocarbon probes in EPR at 30 °C along with the χ calculated from eq 4, using δ_2 = 7.70. The calculated χ values are always significantly lower than the experimental ones, and this difference can be equated to the value of γ in eq 4. The values of γ range from 0.21 to 0.41 and average 0.33, which is definitely outside the experimental error in both χ and δ_2. Using eq 4 with the same value of δ_2 and γ = 0.33, the average value in these experiments, we obtained a value of χ (last column in Table VI) much closer than that from eq 1, probably representing a reasonable approximation to the correct value. However, it does appear that there are consistent differences between the average value of γ with different classes of probe molecules (γ_{av} = 0.39 for linear alkanes vs. 0.27 for aromatic probes), and this may relate to a real difference in this excess entropy term.

The values of δ_2^∞ from the slope and intercept and the corresponding average value of γ are listed in Table V for EPR at 30 and 73 °C for PIP and at 30 °C for PP. There is considerable variation in γ for the three different polymers, but again the average is 0.33. From these data one can conclude that the use of eq 4 with γ = 0.33 should give a reasonable approximation in calculating χ parameters from the solubility parameters of the polymer and probe. Furthermore, if eq 1 is used to estimate δ_2^∞ values from GC data, only the value obtained from the slope should be used, since it does not depend on the value of γ, which may vary from case to case.

From these studies it is concluded that the inverse GC procedure outlined in this and previous papers[2,3] does indeed give a rapid and useful method of estimating the solubility parameter of a polymer, δ_2^∞, at infinite dilution of the probe molecule. Furthermore, extrapolation of the observed χ values to 30 °C appears to be justified in order to calculate δ_2^∞ at temperatures comparable to those at which the solubility parameter is usually measured and reported. Although eq 4 clearly gives a more exact representation of the experimental data than eq 1, the value of δ_2^∞ should not be affected, provided that it is evaluated from the slopes of the relationships given by eq 7 and 11 rather than the intercepts. Except for amorphous polypropylene, the δ_2^∞ values obtained in these experiments are very close to those of the conventional δ_2 values tabulated in the literature. For example, the value for PIP of δ_2^∞ = 7.96 ± 0.10 is very close to that for natural rubber at 25 °C (7.9 to 8.3).[12] Similarly, current values of 7.70 ± 0.11 for EPR and 7.67 ± 0.16 for amorphous PP are very close to that for polyethylene (7.7 to 8.8, mostly near 7.9).[12] Crystalline polypropylene is usually reported to have a solubility parameter of 9.2 to 9.4, which is considerably higher than the value of δ_2^∞ determined in these laboratories for the amorphous polymer. This difference is greater than one would expect from density differences alone and may be related to the experimental problems involved in determining solubility parameters for highly crystalline polymers. The current value indeed seems to be more consistent with what would be expected for a branched alkane polymer without strong crystalline interactions.

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Triplet Energy Migration in Polymer Photochemistry. A Model for the Photodegradation of Poly(phenyl vinyl ketone) in Solution

M. V. Encinas, K. Funabashi, and J. C. Scaiano*

Radiation Laboratory,[1] University of Notre Dame, Notre Dame, Indiana 46556.

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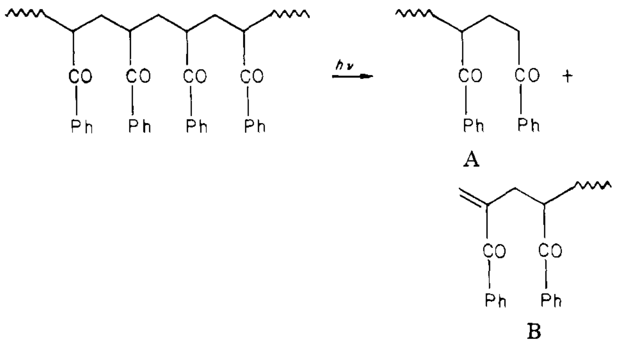
ABSTRACT: Plots of the progress of the degradation of poly(phenyl vinyl ketone) as a function of irradiation time are nonlinear; the effect is the result of triplet quenching by unsaturated end groups generated in the reaction. The process is intramolecular, and from a study of polymers of different initial chain length and application of random walk theory for a one-dimensional lattice it is possible to determine the frequency of triplet energy hopping; the value obtained was ~1 × 10^{12} s^{-1} at 30 °C in benzene. Poly(phenyl vinyl ketone) has a critical chain length of 750 units, this being the average number of chromophores "visited" by the excitation during the triplet lifetime.

The transfer of electronic energy is a process of importance in numerous systems.[2-4] The migration of electronic energy between chromophores of the same type has received attention in solution and in the solid state.[5-9] While singlet energy transfer can occur by several mechanisms, triplet–triplet transfer can only occur by the exchange mechanism, which requires the donor and acceptor groups to be close enough to allow significant overlap of their electron clouds.[5,6]

Energy migration between identical groups is of importance in crystals, glasses, and polymer systems in general. Transfers between truly identical chromophores are virtually impossible to study because the energy transfer process does not lead to an easily observable phenomenon, and most studies make use of small differences between the donor and acceptor molecule. For example, in the case of polymers, the donor and acceptor may differ only in that one of them will be closer to the end of the chain, while they are identical in all other respects. Energy migration of this type is often responsible for the occurrence of chemical or physical processes at a considerable distance from the original excitation site. This phenomenon has important practical implications in the field of photostabilizers, some of which work on the principle of excitation migration toward a suitable energy sink;[10] processes of this type can only be of importance if migration "funnels" the energy toward the sink.

The photochemistry of polymers in the presence of "impurity" traps has been the subject of several studies in films and glasses,[2,11-17] but little is known about the behavior in solution.[18-26]

Poly(phenyl vinyl ketone), PPVK, has been the subject of numerous photochemical studies.[16a,20,21,23-30] The polymer undergoes cleavage via the Norrish type II reaction from the triplet manifold.[20,23]



(1)

When the degradation process is monitored as a function of the irradiation time, the corresponding plot shows significant curvature (Figure 1). This curvature becomes quite evident at extremely low conversions, that is, under conditions where the number of chromophores which have participated in reaction 1 is only a small fraction of the total number of chromophores, typically ~0.1%. Quite clearly, the effect cannot be attributed to the depletion of reactive sites, nor is it the result of UV screening by products or impurities in the polymer (see Results Section). This unusual effect attracted our attention to the problem, which we propose results from intramolecular triplet quenching by α,β-unsaturated carbonyl chromophores of the type shown in fragment B in reaction 1. These groups behave as extremely efficient quenchers; we believe that the high efficiency is the result of fast energy migration, which eventually funnels the energy to the end chromophores in the polymer, effectively leading to quenching by remote energy sinks. The importance of end groups in controlling migration processes had also been recognized

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