linear and characteristic relationship for *each* family of compounds, although Hatada[8] reported only one general linear correlation between these parameters for a whole set of vinyl compounds including styrenes. In spite of the well known[13] poor sensitivity of the $\delta(C_\alpha)$ toward the influence of substituents, the plot of $\delta(C_\alpha)$ vs. e (Figure 2) also indicates a similar trend.

The e values are linearly correlated with Hammett's constants σ;[10] moreover, it is reported that the relationship between ^{13}C chemical shifts and σ values is also linear.[11] It is consequently expected that δ(C) and e values will be correlated by a linear relationship, as demonstrated by the empirical observations.

In our plot (Figure 1), line I correlates $\delta(C_\beta)$ and e values for aliphatic vinyl monomers (22 ppm per e-value unit, the same slope as in Hatada's relationship) and line II correlates $\delta(C_\beta)$ and e values for substituted styrenes (3.5 ppm per e value unit). In Figure 2, the slopes of lines I′ and II″ are respectively 12.5 and 1.25 ppm per e-value unit, confirming the lower sensitivity of $\delta(C_\alpha)$ toward the substituents effects. (In fact, the points corresponding to vinyl aliphatic compounds give a poorer linear fit.)

Apparently, the delocalization of inductive and mesomeric effects of the substituents, in the conjugated system formed by the aromatic ring, overshadows their influence on the vinyl group.

If the literature is unanimous[12] in stressing the interdependence of the Alfrey-Price's e parameter and the polarity of the vinyl bond (induced by the substituent), the weak slope of the $\delta(C_\alpha)$ or $\delta(C_\beta)$ vs. e relationship for substituted styrenes could even raise the question whether there is any correlation in this case. Further work to be published will confirm its existence.

In conclusion, the *linearity* of the different relationships obtained for these two families of vinyl monomers demonstrates the usefulness of ^{13}C NMR spectroscopy as a single and direct tool to estimate the relative reactivity of various vinyl compounds, by using the equations:

$$e(\text{vinyl X}) = \frac{\delta(C_\beta)(\text{ppm/Me}_4\text{Si}) - 113.5}{22}$$

$$e(\text{styrene X}) = \frac{\delta(C_\beta)(\text{ppm/Me}_4\text{Si}) - 115.5}{3.5}$$

where slopes (22 and 3.5) and intercepts (113.5 and 115.5) have been determined by a least-squares technique. Obviously, the method is more useful for aliphatic monomers, since the small slope of the styrene line precludes any precise graphical determination of e.

Acknowledgment. One of us (J.J.H.) is indebted to F.N.R.S. (Belgium) for an "Aspirant" fellowship.

References and Notes

(1) T. Alfrey and C. C. Price, *J. Polym. Sci.*, **2**, 101 (1947); C. C. Price, *ibid.*, **3**, 772 (1948); T. C. Schwan and C. C. Price, *ibid.*, **40**, 457 (1959).
(2) T. Ito, T. Otsu, and M. Imoto, *J. Polym. Sci., Part B*, **4**, 81 (1966).
(3) Yu. D. Semchikov, A. N. Egorovchkin, and A. V. Ryakov, *Vysokomol. Soedin., Ser. B*, **15** (12), 993 (1973).
(4) H. Yuki, K. Hatada, and M. Takeshita, *J. Polym. Sci., Part A-1*, **7**, 667 (1969).
(5) T. Higashimura, S. Okamura, T. Marishima, and T. Yonezawa, *J. Polym. Sci., Part B*, **7**, 23 (1969).
(6) H. Yuki, K. Hatada, and K. Nagata, *Polym. J.*, **1** (2), 269 (1970).
(7) K. Hatada, K. Nagata, and H. Yuki, *Bull. Chem. Soc. Jpn.*, **43**, 3195 (1970).
(8) K. Hatada, K. Nagata, and H. Yuki, *Bull. Chem. Soc. Jpn.*, **43**, 3267 (1970).
(9) K. Hatada, K. Nagata, T. Hasegawa, and H. Yuki, *Makromol. Chem.*, **178**, 2413 (1977).
(10) I. Furukawa and T. Tsuruta, *J. Polym. Sci.*, **36**, 275 (1959).
(11) K. S. Dhami and J. B. Stothers, *Can. J. Chem.*, **43**, 510 (1965).
(12) T. Otsu, *Prog. Polym. Sci., Jpn.*, **3**, 1 (1972).
(13) G. E. Maciel, *J. Phys. Chem.*, **69**, 1947 (1965).

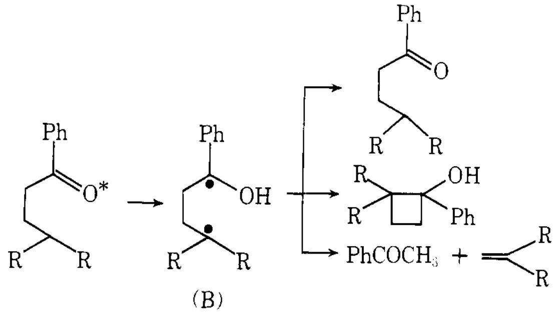
J. J. Herman and Ph. Teyssié*
Laboratory of Macromolecular Chemistry and Organic Catalysis, University of Liège, Sart Tilman, 4000 Liège, Belgium

Received February 15, 1978

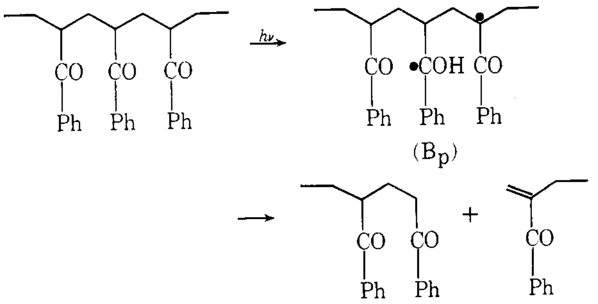
Importance of Intermolecular Biradical Reactions in Polymer Photochemistry. Poly(phenyl vinyl ketone)

The chemistry of the biradicals generated in the Norrish type II reaction has received considerable attention during the last few years.[1-8] Reaction 1 illustrates the mechanism in the case of phenyl alkyl ketones, where the reaction usually occurs solely from the triplet manifold.[9]

The first report on the trapping of B originated in Wagner's laboratory and recognized the possible relevance of the results in polymer chemistry.[1] Three years later, we were able to show that type II biradicals initiate the polymerization of methyl methacrylate quite efficiently.[6] More recently we have pointed out that intermolecular reactions of type II biradicals in polymers could be expected to be of importance.[5,10] While the intermediacy of biradicals in the photochemistry of polymers containing carbonyl groups is widely accepted,[7,11-15] the possibility of their undergoing intermolecular reactions has not been given serious consideration. Reaction 2 illustrates the mechanism of photodegradation of poly(phenyl vinyl ketone), PPVK. The quantum yields of reaction 2 are lower than one,[15] suggesting that a considerable fraction of biradicals (B_p) revert to the parent PPVK.



(1)



(2)

In this communication we report the results of a series of biradical trapping experiments. The details of the measurements, in particular those demonstrating that we are examining biradical processes, are similar to those reported in previous papers.[3,5,6,8] Each of the systems which we describe quite briefly here is interesting by itself and we are currently examining them in detail. However, our immediate aim is not in rigorously detailing the molecular interactions involved in each case, but rather, to demonstrate the necessity of re-

0024-9297/78/2211-0840$01.00/0

Table I
Results from Biradical Trapping Experiments[a]

Substrate	Result
None	$\tau = 76$ ns
SO_2 (0.025 M)	$\tau' = 28$ ns[b]
NO (sat. with $p \sim 39$ Torr)[c]	$\tau' = 59$ ns
t-Bu_2NO	$k_T = 7.5 \times 10^8\ M^{-1}\ s^{-1}$
O_2	$k_T = 1 \times 10^9\ M^{-1}\ s^{-1}$
t-Bu_2CSe (0.02 M)	$\Phi_T \sim 0.005$

[a] In benzene at room temperature. Samples of PPVK were prepared by γ or UV irradiation of benzene solutions of phenyl vinyl ketone, keeping conversions below 25%. The samples were reprecipitated four times using methanol and finally freeze–dried. The UV spectra was similar to that of simple phenyl alkyl ketones. The sample used for these experiments had a molecular weight of 1.3×10^5 based on viscosity measurements. [b] This corresponds to a rate of $\sim 9 \times 10^8\ M^{-1}\ s^{-1}$. [c] Partial pressure in equilibrium with the solution.

Table II
Relative Rates of Propagation in the Polymerization of Methyl Methacrylate

Initiator[a]	Rate	τ_T[b]
None	0.26	
Acetophenone	0.21	3000
Valerophenone	0.43	7
γ-Methylvalerophenone	(1.0)[c]	2
PPVK	0.80	~10[d]

[a] Samples of matched absorbance at 350 nm, with the exception of monomer alone. Irradiated using Rayonet RPR-3500 lamps. [b] Triplet lifetimes in benzene from ref 6, 12, and 14, in nanoseconds. [c] Taken as a reference. [d] Values of 7 and 17 ns have been reported.[12,14]

garding the biradicals generated in the photodegradation of polymers as highly reactive species, capable of undergoing intermolecular reactions.

We have used three different approaches to examine the intermolecular reactivity of B_p: laser photolysis, quantum yield studies, and initiation of polymerization. In the laser photolysis experiments the absorbance due to B_p was monitored directly at 415 nm using the same techniques as described previously.[16] The spectrum of B_p is very similar to that observed for small aromatic ketones[8] and agrees well with that reported by Faure et al.[7] The decay is first order and gives $\tau = 76$ ns in benzene at room temperature. The addition of oxygen, nitric oxide, sulfur dioxide or di-*tert*-butyl nitroxide to the solution causes an increase in the rate of biradical decay, and under these conditions the new lifetimes (τ') are determined by eq 3[8]

$$1/\tau' = (1/\tau) + k_T[T] \qquad (3)$$

where k_T is the rate of interaction with the substrate T. In addition, we usually observe a moderate decrease of the "end-of-pulse" absorption due to the biradical, which reflects quenching of the precursor, i.e., the triplet state. Triplet quenching affects the yield of biradical formation, but not their lifetime. A summary of the results is given in Table I. The rate of reaction for oxygen is significantly slower than for small biradicals;[3] however, it is still an extremely fast process. It should be noted that the interaction with T does not necessarily imply the efficient formation of a new product. In particular, in the case of paramagnetic species this interaction can be expected to result, at least partially, in assisted intersystem crossing and an increase in the yields of fragmentation.[3,17]

The biradicals from PPVK initiate the polymerization of methyl methacrylate very efficiently. This is based on a series of studies similar to those described in a previous report,[6] where the evidence centers around the observation that the initiation is more efficient for the carbonyl compounds with the shorter triplet lifetimes (Table II).[18] The efficiency of PPVK is intermediate between those of valerophenone and γ-methylvalerophenone.

Finally, the biradicals from PPVK can be trapped by di-*tert*-butylselenoketone in experiments similar to those described before for smaller biradicals;[5] however, the yields are considerably smaller. Presumably this reflects the fact that access to the radical sites in polymers is rather difficult for a large molecule like the selenoketone, although a definite answer to this question will require a detailed kinetic study.

Some of the molecules used in this study are not typical components in polymer systems; however, their reactivity is probably not exceptional. Our choice of substrates merely reflects the simplicity of the measurements involved. Further, oxygen and methyl methacrylate are indeed typical components in polymer chemistry. We believe that intermolecular biradical reactions are probably common in polymer chemistry; it is their detection, rather than their occurrence, that is unusual. In fact, it is noteworthy that many polymer additives are chosen precisely because of their high reactivity toward free radical centers; this property makes them obvious candidates for biradical reactions. Processes of this type could also be of importance in other polymers (e.g., polystyrene) where carbonyl chromophores are frequently incorporated during polymerization, processing, and purification.[19]

The preliminary results reported herein suggest that the reaction of biradicals in polymers are somewhat slower than in small molecules; however, it should be noted that the larger biradical lifetime in the case of polymers tends to compensate, at least partially, for this effect.

References and Notes

(1) P. J. Wagner and R. G. Zepp. *J. Am. Chem. Soc.*, **94**, 287 (1972); P. J. Wagner, P. A. Keslo, and R. G. Zepp, *ibid.*, **94**, 7480 (1972).
(2) R. D. Small, Jr., and J. C. Scaiano, *J. Phys. Chem.*, **81**, 828, 2126 (1977); *J. Photochem.*, **6**, 453 (1976/77).
(3) R. D. Small and J. C. Scaiano, *Chem. Phys. Lett.*, **48**, 354 (1977); J. Grotewold, C. M. Previtali, D. Soria, and J. C. Scaiano, *J. Chem. Soc., Chem. Commun.*, 207 (1973); R. D. Small, Jr., and J. C. Scaiano, *J. Am. Chem. Soc.*, in press.
(4) P. J. Wagner and K.-C. Liu, *J. Am. Chem. Soc.*, **96**, 5952 (1974).
(5) J. C. Scaiano, *J. Am. Chem. Soc.*, **99**, 1494 (1977).
(6) M. Hamity and J. C. Scaiano, *J. Photochem.*, **4**, 229 (1975).
(7) J. Faure, J.-P. Fouassier, D.-J. Lougnot, and R. Salvin, *Noveau. J. Chim.*, **1**, 15 (1977).
(8) R. D. Small, Jr., and J. C. Scaiano, *Chem. Phys. Lett.*, **50**, 431 (1977).
(9) P. J. Wagner, *Acc. Chem. Res.*, **4**, 168 (1971).
(10) J. C. Scaiano, E. A. Lissi, and M. V. Encina, *Rev. Chem. Interm.*, in press.
(11) D. J. Carlsson and D. M. Wiles, *Macromolecules*, **2**, 587 (1969); **7**, 259 (1974).
(12) G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 165 (1968); R. J. Golemba and J. E. Guillet, *ibid.*, **5**, 212 (1972); F. Sitek, J. E. Guillet, and M. Heskins, *J. Polym. Sci., Polym. Symp.*, **No. 57**, 343 (1976); J. E. Guillet, *Pure Appl. Chem.*, **49**, 249 (1977), and references therein.
(13) G. Bede, G. Dobrowolski, J. Kiwi, and W. Schnabel, *Macromolecules*, **8**, 9 (1975); J. Kiwi and W. Schnabel, *ibid.*, **9**, 468 (1976); G. Dobrowolski, J. Kiwi, and W. Schnabel, *Eur. Polym. J.*, **12**, 657 (1976).
(14) J. Faure, *Pure Appl. Chem.*, **49**, 487 (1977), and references therein.
(15) M. C. Somersall and J. E. Guillet, *Macromolecules*, **5**, 409 (1972).
(16) The samples were excited using the 337.1 nm (8 ns, 3 mJ) pulses from a Molectron UV-400 nitrogen laser. A pulsed 150W Eimac Xenon lamp was used as a monitoring source. The rest of the system was the same one described previously.[2] The rise time of the detection system was ≤5 ns. All samples were degassed by several freeze–pump–thaw cycles; when the substrates were gases they were added and their partial pressures measured in a mercury free, grease free system.
(17) Y. Kusokawa and M. Anpo, *J. Phys. Chem.*, **79**, 2225 (1975); R. A. Caldwell and D. Creed, *J. Am. Chem. Soc.*, **99**, 8360 (1977).
(18) An excited state process would be expected to be more efficient the longer the triplet lifetime, at least for chromophores with similar characteristics. For a detailed discussion of the experiments involved see ref 5 and 6.
(19) W. Klöpffer, *Eur. Polym. J.*, **11**, 203 (1975).

(20) The research described herein was supported by the Office of Basic Energy Sciences of the Department of Energy. This is Document No. NDRL-1866 from the Notre Dame Radiation Laboratory.

R. D. Small, Jr., and J. C. Scaiano*

Radiation Laboratory,[20] University of Notre Dame,
Notre Dame, Indiana 46556

Received March 24, 1978