reasonable effect: If X_a is near unity, many molecules will have just one very long A block. In contrast, when X_a is small, occurrence of more than one long A block is very unlikely, so that the probability of just one such block per molecule is relatively large. Between these two maxima, then, there is a minimum. The existence of this minimum is implicit in eq 24 which, on differentiation subject to the assumptions of eq 38, predicts a minimum in $X(i, k)$ at $X_a = k/(k + 1)$, *i.e.*, at $X_a = 0.75$ for $k = 3$, where it is indeed observed (Figure 1).

Figure 2 shows that the mole fraction with zero or one long A block varies approximately as the reciprocal of the DP, $\bar{N}$, as predicted by eq 24 (G is roughly proportional to T, the reciprocal of $\bar{N}$, while E is nearly independent of T). The weight fractions, on the other hand, can be seen to vary inversely as the square of $\bar{N}$, except at the lowest $\bar{N}$.

The Photochemistry of Ketone Polymers. IV. Photolysis of Methyl Vinyl Ketone Copolymers

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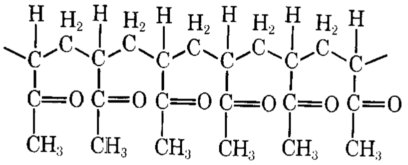
ABSTRACT: Studies have been made of the photolysis of copolymers of methyl methacrylate (MMA) and methyl vinyl ketone (MVK) containing minor amounts of MVK. It is shown that under conditions where there is sufficient molecular mobility (in solution or in the solid phase above T_g), the quantum yield for the process which leads to main-chain scission is 0.20 ± 0.02, nearly an order of magnitude higher than for poly-MVK itself. This is unexpected, because most of the ketone groups are surrounded by MMA units and consequently no γ hydrogens are available to form the cyclic six-membered ring postulated as the transition state for the Norrish type II process. It is suggested that in this case the scission might occur through a seven-membered intermediate, and the δ hydrogen is abstracted. The higher quantum yield for scission of the copolymer indicates that the isolated carbonyl group may be precluded from energy exchange along the polymer chain.

Early studies by Guillet and Norrish[1] and Wissbrun[2] on the photolysis of poly(methyl vinyl ketone) (poly-MVK) demonstrated that the primary photolytic steps involved the Norrish type I and type II reactions typical of low molecular weight aliphatic ketones. At ordinary temperatures the quantum yield for the type II reaction in polymer systems is considerably greater than that for the type I, and the type II reaction represents the major degradation mechanism for polymers containing ketone groups in the backbone or in side chains adjacent to the main chain of the polymer. Recent studies by Guillet and Hartley[3] on the photolysis of ethylene–carbon monoxide copolymers confirm that the type II reaction, which involves a split in the backbone of the chain at the carbon bond α–β to the absorbing carbonyl appears to involve the transient formation of a cyclic six-membered ring involving the hydrogen on the γ-carbon atom. If this is the case, one might expect that the photochemistry of a copolymer system involving methyl vinyl ketone would be affected by the groups adjacent to the ketone monomer in the polymer chain. For example, in poly(methyl vinyl ketone) the general structure is as shown in I. If a central ketone group absorbs a quantum of light, hydrogen is available on the γ-carbon atoms in the chain provided from the adjacent MVK monomer units. However, if one prepares, for example, a copolymer of methyl vinyl ketone and methyl methacrylate containing only a minor amount of MVK, the polymer structure will consist predominantly of units such as shown in II. In this case, as pointed out by Golemba,[4] there are no protons on the γ-carbon atoms which are instead substituted by methyl groups from the MMA units adjacent to the absorbing ketone groups. In this instance, since the six-membered ring transition state can no longer form, one might expect that the quantum yield for the type II photochemical process would be reduced. In the present work, studies were made of the photolytic behavior of copolymers of methyl vinyl ketone with both methyl methacrylate and methyl acrylate, to determine the effect of adjacent monomer units on the photochemistry of the system.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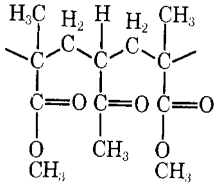
II

Experimental Section

The copolymers were prepared by free-radical polymerization in sealed tubes under vacuum using lauroyl or benzoyl peroxide as initiator. The polymers were dissolved in benzene and reprecipitated several times with methanol to remove catalyst residues and unreacted monomer, then dried to constant weight under vacuum. A summary of the polymers used and their properties is given in Table I.

The irradiation was carried out in benzene solution using the

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(1) J. E. Guillet and R. G. W. Norrish, *Proc. Roy. Soc., Ser. A*, **233**, 153 (1955).

(2) K. F. Wissbrun, *J. Amer. Chem. Soc.*, **81**, 58 (1959).

(3) G. H. Hartley and J. E. Guillet, *Macromolecules*, **1**, 165 (1968).

(4) F. J. Golemba, Ph.D. Thesis, University of Toronto, 1970.

TABLE I
SUMMARY OF POLYMER DATA

Sample	Composition	% MVK	Temp, °C	[Toluene], %	Initiator, %	$\bar{M}_v$[a]	$\bar{M}_n$[b]	$\bar{M}_v/M_n$[c]
1	MMA–MVK	2.9	60	0	1	840,000	170,000	5
2	MMA–MVK	3.0	60	66	2.5	67,000	33,000[d]	2.07
3	Poly-MVK	100	60	66	1	133,000	53,000	2.5

[a] From intrinsic viscosity in benzene, using the relation of Moor and Fort.[6] [b] Estimated from gel permeation chromatography data. [c] From gel permeation chromatography data in THF. [d] By ebulliometry.

TABLE II
CALCULATIONS FOR BIMODAL DISTRIBUTIONS

b	$\frac{(M_w)_0}{(M_n)_0}$	s_1	s_2	$\frac{(\bar{M}_n)_0}{\bar{M}_n} - 1$	$\frac{(\bar{M}_w)_0}{\bar{M}_w} - 1$	$\frac{2(\bar{M}_n)_0}{(\bar{M}_w)_0}$	$\left[\frac{(\bar{M}_w)_0}{(\bar{M}_w)} - 1\right]\frac{2(\bar{M}_n)_0}{(\bar{M}_w)_0}$	Error, %
1	2.00	1.00	1.00	1.000	1.000	1.000	1.000	0.0
2	2.50	0.750	1.50		1.188	0.800	0.950	5.0
2.5	2.90	0.700	1.75		1.338	0.690	0.922	7.8
3.0	3.33	0.666	2.00		1.500	0.602	0.903	9.7
4.0	4.25	0.625	2.50		1.844	0.472	0.870	13.0
5.0	5.20	0.600	3.00		2.200	0.386	0.859	14.1
7.0	7.14	0.571	4.00		2.928	0.280	0.820	18.0
10.0	10.10	0.555	5.5		4.043	0.198	0.800	20.0

apparatus described by Heskins and Guillet.[5] The solutions were sealed under vacuum in a quartz reaction vessel which had a viscometer sealed into the side arm so that viscosity determinations could be made without opening the system to the atmosphere. Determinations of the quantum yields for chain breaking were made by estimating the viscosity molecular weight, $\bar{M}_v$, using the relationship reported by Moor and Fort.[6] Additional determinations were made of both the molecular weight and molecular weight distributions using a Waters Anaprep gel permeation chromatograph calibrated with polystyrene standards in tetrahydrofuran solution. Absolute molecular weights were determined by ebulliometric methods, and calibration of the column for the copolymer systems was obtained by the method of Amerik and Guillet.[7]

The light used was the 3130-Å mercury resonance line from a 250-W medium-pressure mercury arc which was isolated by the use of an interference filter. Light of this wavelength is absorbed by the ketone group but not by any of the other groups in the copolymer system.

Results and Discussion

The copolymers used in this study contained approximately 3% methyl vinyl ketone units, and from the reactivity ratios, one may calculate that, in such a copolymer, the probability of having two MVK units in sequence is very small and in general does not exceed 3% of the ketone groups present. Since the light used is absorbed only by the ketone group, we are therefore able to study the effect of the adjacent groups on the photochemistry of MVK monomer units in the sequence.

When using viscosity methods to determine molecular weight changes, it is usually desirable to use the highest molecular weight possible since the change is more rapid at high molecular weights than at low. Further, the occurrence of side reactions such as the repolymerization process postulated by Guillet and Norrish[1] is less likely in high molecular weight polymers because of the lower concentration of chain ends. The quantum yield for the chain-breaking process in a polymer molecule is given by

$$\phi_s = \frac{w}{(\bar{M}_n)_0} \frac{d\left(\frac{(\bar{M}_n)_0}{\bar{M}_n} - 1\right)}{d(It)} \qquad (1)$$

In this equation, ϕ_s is the quantum yield, which is the number of events occurring per quantum absorbed; $(\bar{M}_n)_0$ is the initial number-average molecular weight; $\bar{M}_n$ is the molecular weight at time t; I is the intensity of light absorbed; the quantity $\{[(\bar{M}_n)_0/\bar{M}_n] - 1\}$ is the number of scissions per original polymer; and w is the weight of polymer in the sample.

When the molecular weight is estimated by viscosity methods, a so-called viscosity-average molecular weight, $\bar{M}_v$, will be determined. This quantity usually lies between $\bar{M}_n$, the number-average molecular weight, and $\bar{M}_w$, the weight-average molecular weight, and is usually much closer to $\bar{M}_w$ than to $\bar{M}_n$. For monodisperse polymers, the three quantities are identical, but for ordinary distributions they will be considerably different. In the present instance, the high molecular weight copolymer studied was shown by gel permeation chromatography to have a rather wide molecular weight distribution, with a polydispersity index, $\bar{M}_w/\bar{M}_n$, of approximately 5. In such a case, we can no longer assume that the ratio $(\bar{M}_n)_0/\bar{M}_n$ is equal to the ratio $(\bar{M}_v)_0/\bar{M}_v$.

An estimate of the error involved in using viscosity molecular weights can be made by the following approximate treatment. A broad molecular weight distribution such as obtained experimentally in this work might be assumed to be made up of a blend of two polymers having most probable distributions.[8] If the number-average molecular weight of one of these distributions is $(\bar{M}_n)_1$ and of the other $(\bar{M}_n)_2$, let us denote the ratio $(\bar{M}_n)_1/(\bar{M}_n)_2$ by b, and let s be the number of bonds broken per original number-average molecular weight of the whole polymer. Let w_1 and w_2 be the weight fractions of the two components of the blend. If we set $w_1 = w_2$ and $b = 5$, then the polydispersity ratio $\bar{M}_w/\bar{M}_n$ will be equal to 5.2, similar to that of our experimental distribu-

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(5) M. Heskins and J. E. Guillet, *Macromolecules*, **1**, 97 (1968).
(6) W. Moor and R. J. Fort, *J. Polym. Sci., Part A*, **1**, 929 (1963).
(7) Y. B. Amerik and J. E. Guillet, manuscript in preparation.
(8) A. M. Kotliar and S. Eichenbaum, *Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem.*, **9**, 341 (1968).

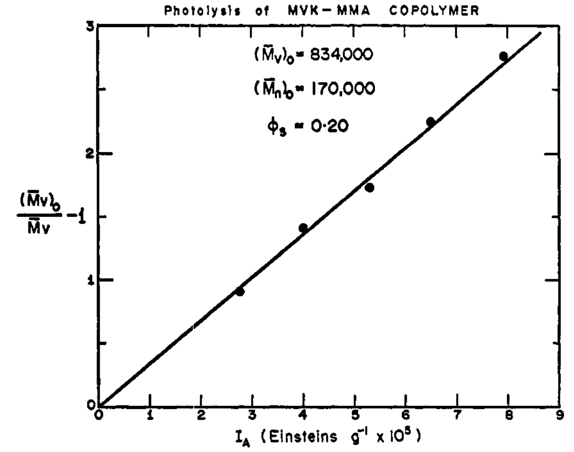


Figure 1. Photodegradation rate for high molecular weight MMA–MVK copolymer (1) containing 2.9% MVK, at 313 nm in benzene solution at 25°, determined by the single-point viscosity method.

tion. From the work of Kotliar and Eichenbaum,[8] the value for $(M_w)_0/\bar{M}_w$ (which we will assume is nearly equal to $(\bar{M}_v)_0/\bar{M}_v$) may be derived from

$$\frac{(\bar{M}_w)_0}{\bar{M}_w} = \frac{(1 + b)}{(1 + s_1)^{-1} + b(1 + s_2)^{-1}} \tag{2}$$

where $s_1 \equiv [(\bar{M}_n)_1/\bar{M}_n]s$ and $s_2 \equiv [(\bar{M}_n)_2/\bar{M}_n]s$. Table II shows the calculated effect of a random-degradation process on the values of $\{[(\bar{M}_w)_0/\bar{M}_w] - 1\}$, $\{[(\bar{M}_n)_0/\bar{M}_n] - 1\}$, $2(\bar{M}_n)_0/(\bar{M}_w)_0$, and on the product $\{[(\bar{M}_w)_0/\bar{M}_w] - 1\}[2(\bar{M}_n)_0/(\bar{M}_w)_0]$, which represents the factor the quantum yield should be divided by if all terms involving $\bar{M}_n$ in eq 1 are replaced by $\bar{M}_w/2$. The values are calculated at a value of s corresponding to one chain break per number-average molecule. It is readily seen that a considerable error is introduced into the two terms of the product by this substitution, but in the opposite sense, so that the total error in the product is less than 20% even when the polydispersity ratio, $(\bar{M}_w)_0/(\bar{M}_n)_0$, exceeds 5 for this simple bimodal distribution. Since most distributions obtained with carefully prepared vinyl polymers will have polydispersity ratios less than this, and the error in the determination of absolute quantum yields seldom is less than ±10%, we conclude that for most purposes, a satisfactory evaluation of the quantum yield for random-chain scission in a polymer can be obtained from the relation

$$\phi_s = \frac{2w}{(\bar{M}_w)_0} \frac{d\left\{\left[\frac{(\bar{M}_w)_0}{\bar{M}_w}\right] - 1\right\}}{d(It)} \tag{3}$$

where $\bar{M}_w$ and $(\bar{M}_w)_0$ are determined from solution viscosity methods by the usual procedures.

Viscosity data on the photodegradation of a high molecular weight copolymer of MMA and MVK are shown in Figure 1. As expected, the change is linear in the amount of absorbed radiation over an extensive range of degradation. Using the polydispersity measured by the gel permeation chromatography method to estimate the number-average molecular weight, the value of the quantum yield is approximately 0.20. This compares with the quantum yield of 0.025 determined by Guillet and Norrish for poly(methyl vinyl ketone) in solution. Because of this unexpectedly high value for the copolymer, it was decided to redetermine the quantum yield with polymers of lower molecular weight using the gel permeation chromatograph to estimate the changes in distribution.

TABLE III
SUMMARY OF MOLECULAR WEIGHT DATA ON DEGRADED MVK–MMA COPOLYMER

Sample	Gel permeation chromatography data M_n	M_w	M_v	M_w/M_n	Exptl[a] $\bar{M}_v$	Exptl $\bar{M}_n$ (ebulliometer)
0	31,800	66,200	61,200	2.08	66,000	32,200
1	30,400	59,800	56,000	1.97	59,800	
2	31,000	49,500		1.60[b]		
3	28,000	55,000	52,050	1.94	55,500	
5	20,200	40,650	37,700	2.01	40,300	21,200
6	14,800	31,600	28,200	2.13	30,100	15,200
7	9,450	17,990	16,400	1.91	20,500	12,600

[a] $\bar{M}_v$ determined in chloroform using the relation $[\eta] = 5.81 \times 10^{-5} \bar{M}_v^{0.79}$. [b] Sample 2 was reprecipitated.

Data obtained by gel permeation chromatography, viscosity, and ebulliometric methods in a series of irradiations are shown in Table III. Typical gel permeation chromatography curves are shown in Figure 2, and the values of $\{[(M_n)_0/M_n] - 1\}$ are plotted as a function of irradiation dose in Figure 3. It is evident from Table III that the molecular weights measured by the three methods agree quite well except at high degrees of degradation, where the molecular weight is low. The ratio $\bar{M}_w/\bar{M}_n$ for the initial low molecular weight polymer is approximately 2 and, as predicted from theory, the polydispersity ratio does not change throughout the degradation. From these data the quantum yield for chain scission is equal to 0.21 from the gel permeation chromatography data. The value calculated from viscosity data only is 0.23, which differs from that from the gel permeation chromatography method by an amount which is only just outside the limits of experimental error. The value calculated from ebulliometry is 0.18.

In view of these increased quantum yields for the copolymer, it seemed desirable to recheck the value of ϕ_s for poly(methyl vinyl ketone) and a low molecular weight polymer was prepared for this purpose by free-radical polymerization. The quantum yield for degradation (10°) was determined in a similar manner using gel permeation chromatography, and ϕ_s was estimated to be approximately 0.04 ± 0.02, which is the same order of magnitude as the value determined by Guillet and Norrish. The large estimated experimental error in this value is due to the fact that an absolute calibration for poly(methyl vinyl ketone) on the gel permeation chromatograph was not available.

The unexpectedly high quantum efficiency for the photolysis of a copolymer which does not contain hydrogens on the γ carbon adjacent to the carbonyl requires that a new mecha-

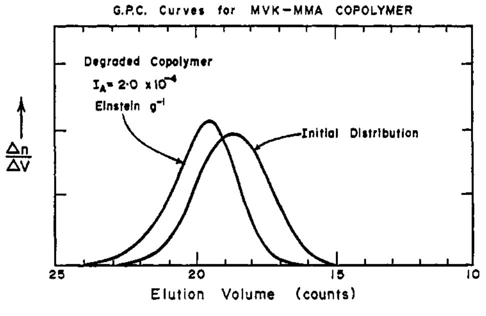


Figure 2. Typical gel permeation chromatography traces for MMA–MVK copolymer (2), and for photodegraded copolymer, at 313 nm in benzene solution at 25° ($I_a = 2.0 \times 10^{-4}$ einstein g^{-1}).

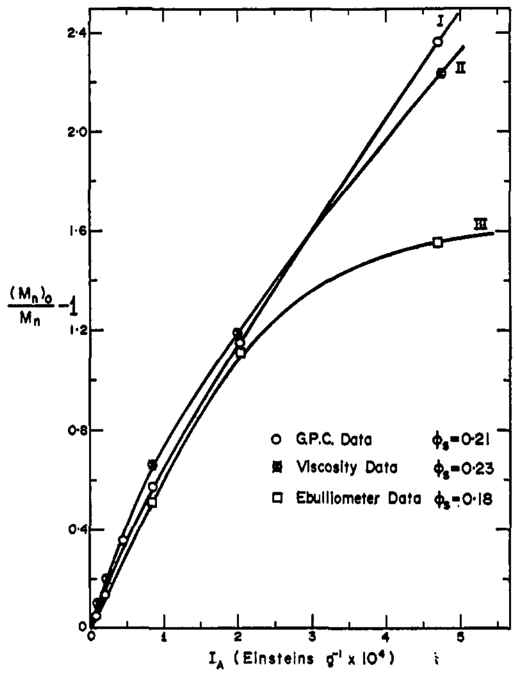
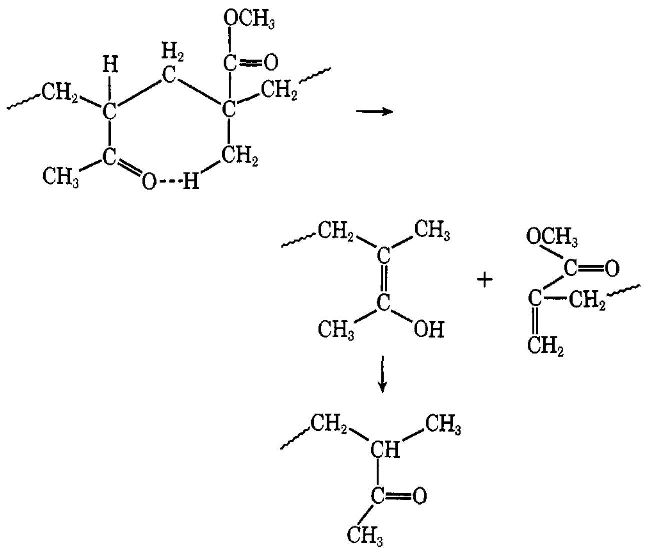


Figure 3. Photodegradation rate of MMA–MVK copolymer (2) (3% MVK) determined by gel permeation chromatography (○), intrinsic viscosity (⊗), and ebulliometric (□) methods. The copolymer was irradiated in benzene solution at 25°, 313 nm.

nism for the photolysis be invoked. It was shown by Hartley and Guillet[3] that the quantum yield for the type II photolysis in ethylene–carbon monoxide copolymers was reduced to 0 at temperatures below the glass-transition temperature. On this basis they assumed that the transition state involved in the Norrish type II process, postulated to be a six-membered ring, could not be formed below the glass transition because of the restrictions on molecular mobility. The MVK–MMA copolymer used in these studies has a glass transition of 75°. If a similar transition state is involved, one would expect that there would be a considerable difference in the quantum yield for the photolysis step in the solid polymer above and below 75°. Accordingly, a series of experiments was carried out to determine the quantum yield for chain breaking in the solid film at 25 and at 86°. The values obtained for ϕ_{II} were 0.0065 at 25° and 0.12 at 86°. Recalling that the value of ϕ_{II} at 25° in solution was 0.21, this is strong evidence that the process involving main-chain scission requires molecular mobility in order to form the transition state.

We suggest, therefore, that by an analogy with the type II mechanism, a cyclic seven-membered transition state is involved in the main chain-breaking process which results in scission at the β–γ carbon–carbon bond in the polymer chain and that the formation of such a cyclic seven-membered intermediate is inhibited at temperatures below the glass transition in the solid polymer. The process can be described as shown in eq 4. A similar reaction has been shown in low molecular weight ketones which contain both γ-hydrogen atoms and δ-hydrogen atoms.[9] In this case, a similar process occurs and the quantum yields do not seem to be substantially different from those in the conventional type II process. On this basis, we assume that, although the formation of a seven-membered ring, is less favored than that of a six-membered ring, it is still sufficiently probable to



provide an efficient route for photochemical reaction. Although absorption bands attributable to double bonds can be observed in the ir spectra of irradiated films, this mechanism must be considered as tentative until it is possible to confirm the exact nature of the end groups formed in the scission reaction.

The next problem is to explain why the quantum yield for chain breaking of the copolymer is greater than that of the homopolymer poly-MVK. A possible answer can be obtained by consideration of the structure of poly(methyl vinyl ketone). In this case, the absorption of light by a ketone chromophore at any position along the chain will result in the formation of an excited carbonyl group. This carbonyl group will be in close proximity to a series of other ketone groups having similar energy levels and located at regular intervals along the backbone of the polymer chain. On the other hand, an excited carbonyl in the MMA–MVK copolymer will be surrounded by methyl methacrylate ester groups, which have much higher energy levels. The lifetimes of the triplet and singlet excited states of aliphatic ketone groups in the polymer have been shown by Heskins and Guillet to be of the order 10^{-8}–10^{-9} sec.[10] During this time, the chain will undergo a number of rotations which will permit the alignment of the carbonyl groups to within close proximity to the excited carbonyl. This would permit energy transfer by an exchange mechanism to occur between adjacent carbonyl groups, and by this mechanism the excitation energy may move along extensive distances of the polymer chain.

A further effect of this will be a relaxation of the rules regarding the forbidden $S_1 \rightarrow S_0$ and $T_1 \rightarrow T_0$ transitions by nonradiative processes. This will allow a more favorable route for the conversion of electronic to vibrational energy and thus reduce the quantum yield for the competing photochemical process. In the case of the MMA–MVK copolymer, however, each ketone group will be surrounded by an ester group, and the energy levels of both the triplet and singlet of the ester carbonyl will lie above those for the corresponding levels of the ketone; hence, energy transfer to the ester carbonyl will be endothermic and therefore of unlikely occurrence. The value of ϕ_s for the chain-breaking process is very similar to the value of ϕ_{II} = 0.20 which was obtained for a series of long-chain aliphatic ketones by Golemba and Guillet,[11] and this appears to be characteristic

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(9) D. J. Coyle, R. V. Peterson, and J. Heicklen, *J. Amer. Chem. Soc.*, 86, 3850 (1964).

(10) M. Heskins and J. E. Guillet, *Macromolecules*, 3, 224 (1970).

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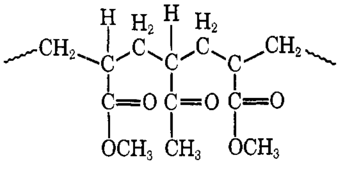
for the type II process in isolated methyl ketone groups in polymer systems.

If this explanation is correct, one would expect, therefore, to observe a similar increase in quantum yield for copolymers containing γ hydrogens. Accordingly, a copolymer was made of methyl vinyl ketone with methyl acrylate. In this case, the polymer structure would have the sequence shown in III. Photolysis of this copolymer in benzene solution by a similar method gave a value for ϕ_s of approximately 0.2,[12] which again is substantially higher than for poly-MVK.



III

On the basis of these results, we suggest that the quantum yield for main-chain scission in vinyl copolymers containing pendant methyl ketone groups adjacent to the main chain will be approximately 0.2 in systems where the carbonyl is isolated from similar groups along the chain and where the molecular mobility is high. In solid polymers, the quantum yield will be reduced to very low values at temperatures below the glass-transition temperature of the polymer because of the restriction in molecular mobility. We suggest that the scission mechanism in such copolymers involves the breaking of either α–β or β–γ carbon–carbon bonds through an intermediate transition state consisting of either a six- or a seven-membered ring through a γ- or δ-hydrogen atom. We further conclude that transfer of excitation energy along a polymer chain will be possible in systems where similar chromophores are located in adjacent positions along the backbone. When such is the case, one may expect to get substantial changes in the quantum yields for the observed photochemical processes.

Acknowledgment. The authors wish to acknowledge the generous financial assistance of the National Research Council of Canada and the many helpful discussions with F. Golemba, M. Heskins, and E. Dan.

[12] E. Dan and J. E. Guillet, unpublished work.

The Crystalline Morphology of Poly(*N*-vinylcarbazole)[1]

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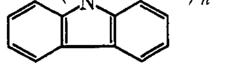
ABSTRACT: The crystalline morphology of poly(*N*-vinylcarbazole), a polymer which exhibits interesting electrical properties, has been examined by optical microscopy, electron microscopy, electron diffraction, and X-ray diffraction. The unsheared polymer crystallized into fragmented "pseudo-spherulitic" structures at temperatures above 285° which then melted between 347 and 351°. Crystallization was markedly shear dependent, and shear-induced crystallization was noted at temperatures as low as 230°. The morphology of such crystallizations was characterized by bundles of fibrous entities approximately 250 Å in diameter oriented parallel to the shear direction, and bore a striking resemblance to the fibrous texture reported for polytetrafluoroethylene. Resultant poor mechanical properties were attributed to weak interfibrillar bonding. Two distinct single crystal morphologies were grown from dilute solution using several solvent systems. Below 115° rod-shaped crystals (which appear to be extended chain structures) were formed, while above approximately 115°, flat thin lamellar (presumably chain-folded) crystals were realized. Because of the large bulky pendant groups attached to the polymer, it is postulated that below approximately 115° the polymer in solution is too stiff to chain fold, while above 115° chain folding is possible. Electron diffraction from solution grown single crystals suggest that PVK molecules are isotactic, and form a 3/1 helical array in a hexagonal packing with $a_1 = a_2 = a_3 = 12.30$ Å and $c = 7.44$ Å.

Poly(*N*-vinylcarbazole) (PVK) was used very heavily during World War II as a substitute for mica because of its good dielectric properties and heat resistance. While further research into the polymer's high-temperature resistance continued after the war, its extreme brittleness and tendency to cause exzema-type rashes on personnel handling it has resulted in a drastic decrease in production.[2a] Interest today centers largely on PVK's electrical properties. Hoegl, *et al.*,[2b] identified the photoconductive properties of the polymer which have since been studied in detail.[3-5] Charge-transfer complexing between PVK and iodine has been reported by Hermann and Rembaum.[6] From a manufacturing point of view, the polymer is difficult to handle by conventional molding techniques, but is tractable in several organic solvents. The solution properties of PVK have been described by Naghizadeh and Springer[7] and more recently by



poly (*N*-vinylcarbazole) repeat unit

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[1] Presented in part at the American Physical Society Meeting, Dallas, Texas, March 1970.

[2] (a) J. A. Brydson, "Plastics Materials," Van Nostrand, Princeton, N. J., 1966; (b) H. Hoegl, O. Sus, and W. Neugebauer, West German Patent 1,068,115 (1957).

[3] H. Hoegl, *J. Phys. Chem.*, **69**, 755 (1965).

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[7] J. Naghizadeh and J. Springer, *Kolloid-Z. Z. Polym.*, **215, 1**, 21 (1967).