

Photodegradation of chloromethyl vinyl ketone polymer and copolymers with styrene and α -methylstyrene

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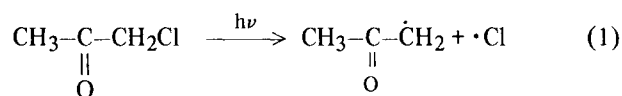
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The photodegradation behaviour of chloromethyl vinyl ketone (CMVK) polymer has been compared with that of polymers of methyl and tertiary butyl vinyl ketones, MVK and t-BVK, respectively. The results obtained for poly(CMVK) showed that the quantum yields of main chain scission in dioxane and of the Norrish type I reaction (ϕ_I) in film were 0.18 and 0.61 times, respectively, greater than those of poly(MVK), while ϕ_I for poly(t-BVK) was about 19 times that of poly(MVK). It was also found that the photolysis of poly(CMVK) produced a considerable amount of hydrogen chloride and its quantum yield (ϕ_{HCl}) was higher than ϕ_I , i.e. $\phi_{HCl}/\phi_I = 1.7$. This was attributed to the intramolecular transfer of photoexcited energy from the ketone chromophore to the adjacent chloromethyl group. The existence of such a reaction was supported from the remarkable acceleration of the photopolymerization of methyl methacrylate. The photodegradation mechanism of poly(CMVK) is discussed, in the light of the results obtained above and from the studies on quenching and on the photodegradation of CMVK copolymer.

INTRODUCTION

α -Haloketones belong to a class of compounds which undergo characteristic reaction in the field of photochemistry¹. For example, the photolysis of chloroacetone with light of wavelength 313 nm has been studied in detail by Strachan and Blacet². They showed that the primary process of this reaction was the dissociation of the C-Cl bond:



Because of the ease of formation of such reactive radicals, even using light of higher wavelength, α -haloketones have been employed in organic synthesis as a useful radical source³.

On the other hand, the photochemistry and photophysics of polymers containing the α -haloketone moiety have been little known. In this paper, the preparation of the polymer of chloromethyl vinyl ketone (CMVK) is described, and its photochemical and photophysical processes are investigated.

The photodegradation of tert-butyl vinyl ketone (t-BVK) polymer and copolymer has been reported in a previous paper⁴. Those results are compared with the ones obtained from the present study.

EXPERIMENTAL

Vinyl ketone monomers were prepared according to the method described in the previous paper⁵. Radical polymerization of these monomers was accomplished using α,α' -azobisisobutyronitrile as an initiator. Gas analysis was carried out by the method of Wissbrun⁶. Photodegradation of

a copolymer was carried out at fixed concentration (0.2 g/dl), and all other experimental procedures were similar to those described in the previous paper⁴.

RESULTS AND DISCUSSION

Quantum yield of main chain scission (ϕ_{cs}) of poly(CMVK)

To evaluate the number-average molecular weight (\bar{M}_n) of poly(CMVK) from viscosity measurement in dioxane, the k_H constant in the Huggins equation, $\eta_{sp}/c = [\eta] (1 + k_H[\eta]c)$, and K_m and α constants in the Mark-Houwink-Sakurada equation, $[\eta] = K_m \bar{M}_n^\alpha$, were determined. In a similar manner to the previous paper, the values of k_H , K_m , and α for poly(CMVK) were determined to be 0.18, 5.15×10^5 dl/g, and 0.77, respectively. For methyl vinyl ketone (MVK) polymer, such values of k_H , K_m , and α were also determined to be 0.27, 4.92×10^5 dl/g, and 0.81, respectively.

To estimate the quantum yield of main chain scission (ϕ_{cs}) of a polymer, the relationships between the number of main chain scissions per original polymer $[(\bar{M}_{no}/\bar{M}_n) - 1]$ and exposure time (t) were examined both for poly(CMVK) and poly(MVK), where \bar{M}_{no} and \bar{M}_n are number-average molecular weights of the polymer before and after degradation. The plots of $(\bar{M}_{no}/\bar{M}_n) - 1$ with t are shown in Figure 1. The value of ϕ_{cs} was determined from this Figure according to equation (2);

$$(\bar{M}_{no}/\bar{M}_n) - 1 = \phi_{cs} \bar{M}_{no} I t \quad (2)$$

where I is the light intensity absorbed by polymer.

Since both polymers show identical ultra-violet absorption spectra as shown in Figure 2, and equal irradiation doses are

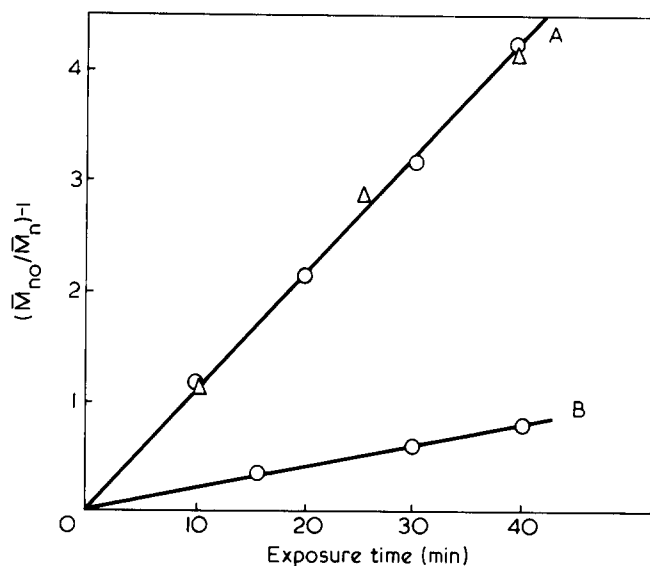


Figure 1 Photodegradations of poly(CMVK) and poly(MVK); A, poly(MVK) measured by viscometry (○) and directly (△); B, poly(CMVK)

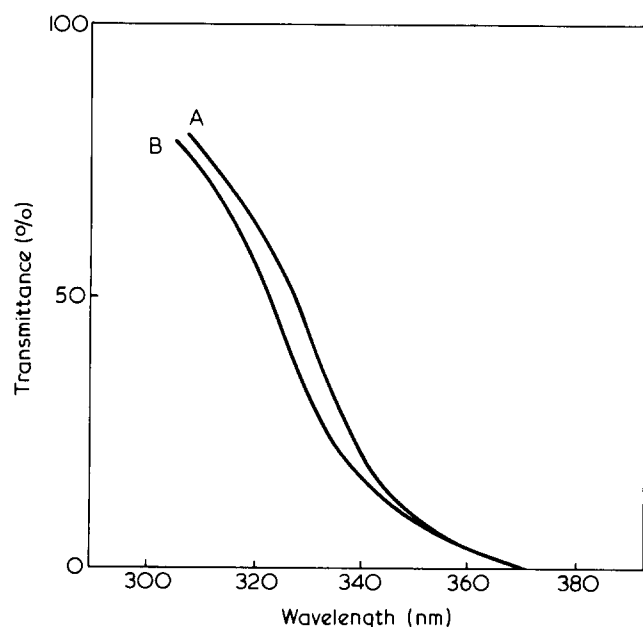


Figure 2 Ultra-violet spectra of poly(CMVK) and poly(MVK) in dioxane; A, poly(CMVK); B, poly(MVK)

used, it is assumed that the value of I in equation (2) is approximately equal for both polymers.

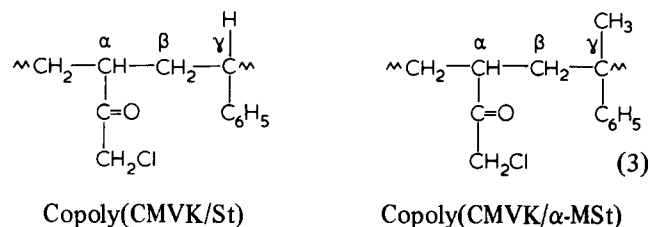
Table 1 summarizes the \bar{M}_{no} and relative ϕ_{cs} values of poly(CMVK) and poly(MVK). From this Table, it appears that poly(CMVK) is more stable to light for the reduction of molecular weight than poly(MVK), and also than poly(*t*-BVK)⁴. Using the absolute ϕ_{cs} value of 0.025 for poly(MVK)⁶, the absolute ϕ_{cs} value of poly(CMVK) is calculated to be 0.0046.

Photodegradation of copolymers

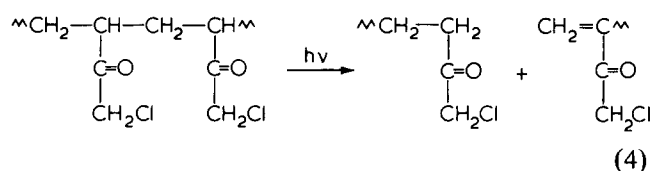
To confirm the mechanism of photodegradation, the copolymers of CMVK with styrene (St) and α -methylstyrene (α -MSt) were photolysed under irradiation of light above 300 nm. In both these cases, the random sequences of monomer units in the copolymers were deduced from the examination of their monomer reactivity ratios which were shown in the previous paper⁵.

Figures 3 and 4 show the relationships between the viscosity numbers of the copolymers and exposure time for the photodegradations of copoly(CMVK/St) and copoly(CMVK/ α -MSt), respectively. In both cases, it is observed that the decreasing tendency in viscosity numbers with irradiation time, increases with increasing CMVK content. In addition, its tendency is larger in the copolymer with St than with α -MSt.

This is explained by the difference in the copolymer structure, i.e. the copolymer with St has a hydrogen atom on γ -carbon of CMVK unit, while the copolymer with α -MSt contains no hydrogen atom in such a position. This structural difference is shown in equation (3).



These results suggest the participation of the Norrish type II photoelimination in the photodegradations of both copolymers, as well as poly(CMVK) [equation (4)].



Gas analysis

When light of high intensity with a wavelength above 300 nm is used to irradiate the film of poly(CMVK), hydro-

Table 1 Relative ϕ_{cs} values of poly(CMVK) and poly(MVK)

Polymer	ϕ_{cs}	\bar{M}_{no}
Poly(CMVK)	0.18	150 000
Poly(MVK)	1.0	102 000

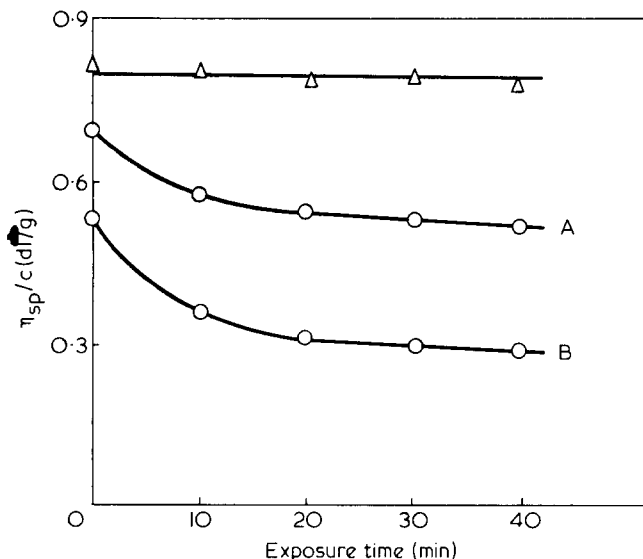


Figure 3 Photodegradation of copoly(CMVK/St): ○, copoly(CMVK/St) composed of 42/58 (A) and 58/42 (B); △, polystyrene

gen chloride, carbon monoxide, and aldehyde are detected as main products.

Table 2 summarizes the gas analyses evolved in the photolyses of poly(CMVK) and poly(MVK), as well as poly(t-BVK). From this Table, the quantum yield of the Norrish type I reaction (ϕ_I) of poly(CMVK) is found to be 0.61 times lower than that of poly(MVK), in which ϕ_I are given as minimum values because of the occurrence of the addition of radical produced such as acetyl radical to the C—C double bond formed by the type II elimination. It is noted that poly(CMVK) produces a considerable amount of hydrogen chloride, i.e. about 3.5 times more than the amount of carbon monoxide or aldehyde. Thus, the quantum yield of the production of hydrogen chloride (ϕ_{HCl}) is larger than ϕ_I as follows (equation 5):

$$\frac{\phi_{HCl}}{\phi_I} = \frac{\phi_{HCl}}{\phi_{CO} + \phi_{aldehyde}} = 1.7 \quad (5)$$

where ϕ_{CO} is the quantum yield of the production of carbon monoxide.

The absolute ϕ_I value of poly(MVK) has been reported to be 0.04 in dioxane at 25°C with light of 313 nm⁷. Using this value, the absolute ϕ_I and ϕ_{HCl} values of poly(CMVK) are calculated to be about 0.024 and 0.041, respectively, although the difference between film and solution states must be considered.

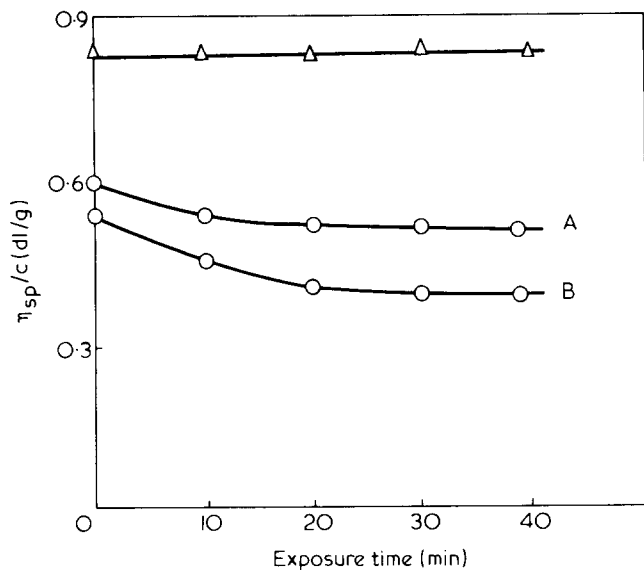
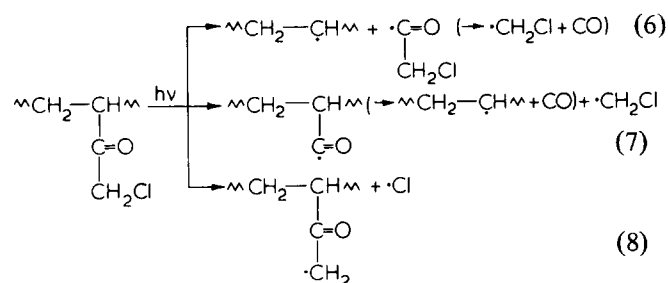


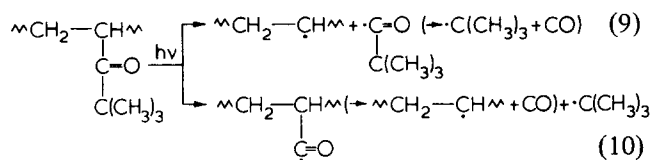
Figure 4 Photodegradation of copoly(CMVK/α-MSt): O, copoly(CMVK/α-MSt) composed of 51/49 (A) and 62/38 (B); Δ, polystyrene

From these facts, the reactions (6), (7) and (8) are expected to be the primary processes in the photolysis of poly(CMVK), in addition to the Norrish type II photoelimination.



Reaction (7) seems to be less probable for the reason which was mentioned in the case of poly(MVK)^{7,8}. Thus, under these conditions, the Norrish type I reaction (equation 6) must compete with the favourable reaction (8). Therefore, it is concluded that the reactions (6) and (8), and also the type II elimination, should compete with one another in the primary process of the photochemical reaction of poly(CMVK).

On the other hand, the ratio of aldehyde to carbon monoxide for poly(t-BVK) is very small as can be seen in Table 2. It has been reported that the ease of decarbonylation of acyl radical depends significantly on the stability of the alkyl radical produced⁹, and that at moderately low temperature the acyl radical produced from trimethylacetaldehyde undergoes complete decarbonylation¹⁰. Therefore, the result obtained for poly(t-BVK) is not surprising. The features of the Norrish type I reaction of poly(t-BVK) can be shown in equations (9) and (10):



The ϕ_I value of poly(t-BVK) is about 19 times larger than that of poly(MVK) as can be seen in Table 2. This suggests that reaction (10) might be expected to be predominant over reaction (9), since the rate of reaction (9) seems to be not very different from that of the following reaction involving poly(MVK) (equation 11):

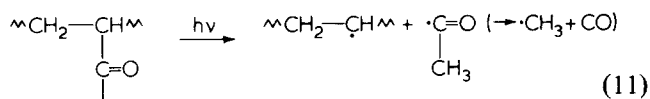


Table 2 Gas analyses of poly(CMVK), poly(t-BVK), and poly(MVK) in film at 30°C

Polymer	Time (min)	CO (x 10 ⁶ mol)	Aldehyde (x 10 ⁶ mol)	HCl (x 10 ⁵ mol)	Minimum ^a ϕ_I
Poly(CMVK)	15	7.3	8.0	2.47	—
	30	15.9	15.9	5.30	0.61
Poly(t-BVK)	15	480	2.0	—	—
	30	951	3.7	—	18.7
	60	1210	5.0	—	—
Poly(MVK)	15	1.6	24.9	—	—
	30	3.0	48.0	—	1.0

^a $\phi_I = \phi_{CO} + \phi_{aldehyde}$. The minimum ϕ_I value shows relative value

Table 3 Photopolymerization of methyl methacrylate in the presence of ketone polymers and low molecular weight ketones^a

Ketone	Time (h)	Yield (%)
Poly(CMVK)	1.0	6.54
Poly(t-BVK)	1.0	7.93
Poly(PVK)	1.0	1.62
Poly(MVK)	1.0	1.29
CH ₃ COCH ₂ Cl	1.2	3.20
CH ₃ COC(CH ₃) ₃	1.2	2.86
C ₆ H ₅ CO(CH ₂) ₃ CH ₃	1.2	0.64
CH ₃ CO(CH ₂) ₃ CH ₃	1.2	0.72
None	1.2	0.43

^a Polymerization conditions: [ketone] = 0.01 mol/l, MMA (4 ml) + dioxane (2 ml); ^b PVK, phenyl vinyl ketone

The absolute ϕ_1 value for poly(t-BVK) is calculated to be 0.75 in a similar manner. In these experiments, an experimental error seems to be, at least, about 20%. Such a high value of ϕ_1 for poly(t-BVK) appears not to deviate much from that obtained from low molecular weight ketones such as tert-butyl n-propyl ketone and n-butyl tert-butyl ketone¹¹.

From the reactions (6), (8), (9), and (10), it was indicated that the irradiation of poly(CMVK) or poly(t-BVK) produced the reactive radicals. Therefore, it can be expected that poly(CMVK) as well as poly(t-BVK) induces the photopolymerization of vinyl monomer such as methyl methacrylate (MMA) to give a graft copolymer.

Table 3 shows the result obtained from the photopolymerization of MMA in the presence of vinyl ketone polymers and of their model compounds. From this Table, it is clear that poly(CMVK) and poly(t-BVK) can markedly accelerate the polymerization of MMA. This suggests that the reactions (6), (8), (9) and (10) do occur. It is also found that all ketone polymers induce the polymerization of MMA in high yield compared with the corresponding low molecular weight model compounds. This may be due to the ease of radical dissociation in the ketone polymers used, since the radical produced is secondary for polymer, but primary for model compound. To compare the ϕ_1 value obtained from such gas analysis with these experiments of graft copolymerization, the rate of photopolymerization of MMA (R_p) in the presence of vinyl ketone polymer was determined from the initial slope of the time-conversion curve of such a polymerization. For example, R_p was estimated to be 13.7×10^{-5} and 2.10×10^{-5} mol/l sec in the cases of poly(t-BVK) and poly(MVK), respectively. From both R_p values obtained, the ratio of ϕ_1 of poly(t-BVK) to that of poly(MVK) was determined to be 17 with an error of about 30%, in a similar manner to Guillet and Norrish⁷. This value obtained is in fairly good agreement with that obtained from the evolved gas analysis.

Quenching study

To clarify the photoexcited state induced during the photodegradation of poly(CMVK), a quenching study with 2,5-dimethyl-2,4-hexadiene (DMHD) was carried out under similar experimental conditions to the previous work⁴.

Figure 5 shows the plot by the simple Stern-Volmer equation (equation 12):

$$\frac{\phi_0}{\phi} = 1 + k_q \tau_T [\text{DMHD}] \quad (12)$$

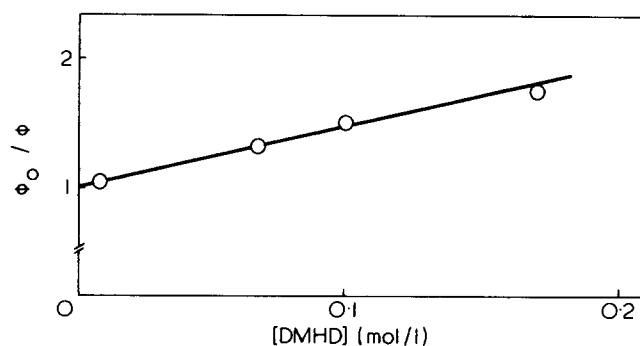


Figure 5 Stern-Volmer plot for the photodegradation of poly(CMVK) using 2,5-dimethyl-2,4-hexadiene (DMHD) in dioxane at 366 nm

in which ϕ_0 , ϕ are quantum yield in the absence and presence of the quencher DMHD, and τ_T is the triplet lifetime of the donor molecule in the excited state on quenching in the absence of the quencher, and k_q is the rate constant for bimolecular quenching.

As can be seen from this Figure, the expected straight line is attained at this diene concentration. The slope has a value of 5 l/mol. Wettack and coworkers¹² have shown that some quenching of the singlet state may also occur at high diene concentration, but it seems unlikely that this would be a factor at the concentration used in this work. In this system, it may also be improbable that only one excited state such as the triplet state induces the main chain scission of poly(CMVK), since the photoexcited state induced main chain scission of poly(CMVK) is expected to be similar to that of poly(MVK), in which both singlet and triplet states take part. Moreover, the reversible energy transfer between photoexcited triplet states of the quencher and poly(CMVK) seems to be unlikely, since the difference of excited triplet energy between DMHD quencher and poly(CMVK) is expected to be around 60 kJ/mol.

The low value of $k_q \tau_T$ obtained, therefore, seems to be rationalized by the effective energy transfer from the photoexcited ketone chromophore of poly(CMVK) to the chloromethyl group adjacent to the ketone group.

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