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Thermal Degradation Behavior of Vinyl Ketone Polymers and Copolymers with Styrene

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ABSTRACT

Thermal degradation behavior of six alkyl vinyl ketone (RVK) polymers and copolymers with styrene was investigated by means of infrared spectrometry (IR), thermogravimetry (TG), derivative TG (DTG), and differential scanning calorimetry (DSC). The observed TG curves of the RVK polymers changed with both structure of their substituents and initiators used, and the temperature of the beginning of weight loss for the radical polymers increased in the order: poly(methyl isopropenyl ketone) < poly(methyl vinyl ketone) < poly(ethyl vinyl ketone) < poly(isopropyl vinyl ketone) < poly(tert-butyl vinyl ketone). From the infrared spectral determination of thermally degraded polymers, the formation of a cyclized structure was observed. It was also found from the results of thermal degradation of the RVK copolymers with styrene at 210°C that the formation of such a cyclized unit tended to increase in the order: tert-butyl vinyl ketone < isopropyl vinyl ketone < ethyl vinyl ketone < methyl vinyl ketone.

INTRODUCTION

Marvel and co-workers [1, 2] found that when the polymers of methyl vinyl ketone (MVK) and methyl isopropenyl ketone (MIPK) were heated, water which was calculated from the head-to-tail structure was eliminated by the aldol condensation to give cyclohexenone derivatives. Subsequently many workers [3-6] reconfirmed this observation from elementary analysis [4, 5] infrared [3, 5] and ultraviolet spectroscopy [4, 5], thermogravimetric analysis [6], and thermal volatilization analysis [5]. Recently the effect of stereoregularity on thermal degradation of poly(MVK) has been reported by Matsuzaki et al. [7].

As stated above, the thermal degradation behavior of poly(MVK) and poly(MIPK) has been well investigated, but that of other RVK polymers and copolymers has not been studied in detail up to the present time. In previous papers [8-10] we reported on investigations of the homo- or copolymerization [8] and cyclodimerization [9] of various RVK monomers and on the photodegradation of these polymers [10].

In the present paper, the effects of alkyl groups in RVK polymers and copolymers with styrene obtained by radical and anionic initiators on their thermal degradations were investigated by means of infrared spectroscopy (IR), thermogravimetry (TG), derivative TG (DTG), and differential scanning calorimetry (DSC). RVK monomers used are MVK, MIPK, ethyl vinyl ketone (EVK), isopropyl vinyl ketone (IPVK), tert-butyl vinyl ketone (t-BVK), and phenyl vinyl ketone (PVK).

EXPERIMENTAL

Preparation of Polymer

Six PVK monomers were prepared according to the procedure described in a previous paper [8]. Radical polymerizations of these monomers were performed with AIBN at 60°C. Anionic polymerizations were also carried out with n-butyllithium (BuLi), aluminum isobutylate ($\text{Al}(\text{i-Bu})_3$), and potassium tert-butoxide (t-BuOK) at 0 and 90°C. BuLi and $\text{Al}(\text{i-Bu})_3$ used were commercial anhydrous products, while t-BuOK was synthesized by the reaction of tert-butanol with potassium. In the polymerizations with t-BuOK, N-phenyl- β -naphthylamine was added to the polymerization mixture in order to prevent radical polymerization.

After polymerization for a given time, the polymerization mixture was poured into a large amount of methanol when AIBN was used; when polymerization was with an anionic initiator, methanol containing a small amount of hydrochloric acid was used as precipitant, followed by reprecipitation into diethyl ether.

Analysis of Thermal Degradation

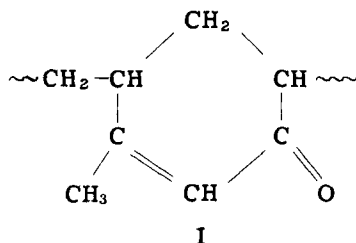
TG and derivative TG (DTG) were recorded on Shimadzu thermogravimeter, Model TG-20. The heating rate was 10°C/min, and a dynamic nitrogen atmosphere of 50 ml/min was used. DSC measurement was carried out by Perkin-Elmer Model DSC-1 instrument.

Thermal degradation of the copolymers of RVK with styrene were carried out at 210°C for 6 hr under a nitrogen atmosphere.

RESULTS AND DISCUSSION

Polymerization of PVK

Table 1 shows the results of radical and anionic polymerizations of six RVK. All RVK monomers were observed to polymerize easily under these conditions. All of polymers and copolymers with styrene obtained with AIBN were colorless powders, but the MVK polymers obtained by anionic initiators showed a pale-yellow color, although the other RVK polymers were colorless powders. Such coloration of the MVK polymers seemed to be due to the formation of a cyclized structure (I) from their IR spectra. In the polymers obtained anionically from EVK, IPVK, *t*-BVK, and PVK, the absorption band due to



a cyclized structure was not observed. However, the anionically obtained polymers of MIPK showed a pale-yellow color due to the

TABLE 1. Polymerizations of RVK with Various Initiators in Toluene

RVK	Initiator	Temperature (°C)	Time (day)	Yield (%)
MVK	AIBN	60	0.5	55.3
	BuLi	0	2	22.0
	t-BuOK	0	3	88.1
	t-BuOK	90	0.3	85.3
	Al(i-Bu) ₃	0	3	54.7
EVK	AIBN	60	0.5	52.0
IPVK	AIBN	60	0.5	52.0
	t-BuOK	0	3	45.1
	t-BuOK	90	0.3	39.6
	Al(i-Bu) ₃	0	3	16.6
t-BVK	AIBN	60	0.5	57.8
	BuLi	0	2	76.3
	t-BuOK	0	3	69.7
	t-BuOK	90	0.3	65.5
	Al(i-Bu) ₃	0	3	61.3
PVK	AIBN	60	0.5	64.2
	BuLi	0	2	12.9
	Al(i-Bu) ₃	0	3	79.5
MIPK	AIBN	60	0.5	22.5
	t-BuOK	0	3	22.1
	t-BuOK	90	0.3	27.8
	Al(i-Bu) ₃	0	3	22.5

^a Polymerization conditions: [AIBN] = 5.5×10^{-3} mole/liter; [BuLi] = [t-BuOK] = [Al(i-Bu)₃] = 1.5 mole %; [N-phenyl- β -naphthylamine] = 2 mole %; [toluene] = ca. 50 mole %.

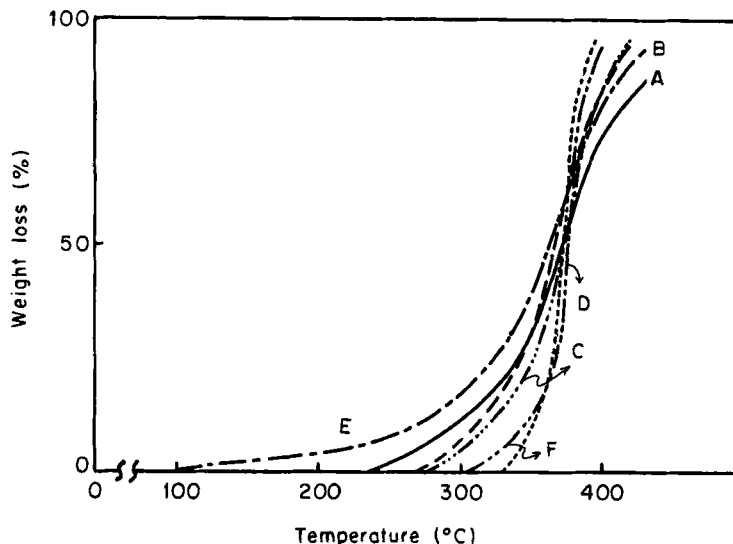


FIG. 1. Thermogravimetric curves of the RVK polymers obtained by AIBN (10 C/min, in nitrogen): (A) poly(MVK); (B) poly(EVK); (C) poly(PIVK)/ (D) poly(*t*-BVK); (E) poly(MIPK); (F) poly(PVK).

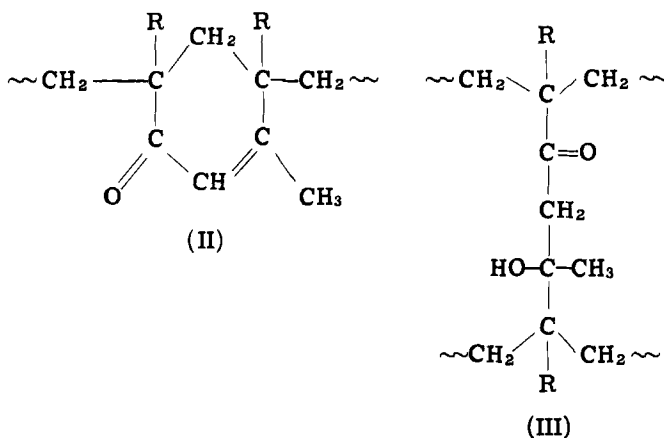
formation of the cyclized unit. Therefore, it seemed that the methyl group in RVK was more reactive to cyclization than the other alkyl groups.

The polymers of *t*-BVK obtained by anionic initiators in toluene contained some fraction insoluble in benzene. The IR spectra of the benzene-insoluble polymers showed new absorption bands at 1330 and 1100 cm^{-1} which were characteristic of isotactic structure [3, 4], indicating the formation of isotactic polymer from *t*-BVK by anionic initiators, as described in a previous paper [10].

Thermal Stability of RVK Polymers Obtained with AIBN

Figure 1 shows the TG curves of the RVK polymers obtained by AIBN. From Fig. 1 it is clear that poly(MIPK) is the most unstable and poly(MVK) is next unstable, as compared with the other RVK polymers. Such result seems to be related with the pale-yellow

coloration in these polymers obtained by anionic polymerization, as mentioned above. Therefore, thermal instability of these polymers seems to originate from easy formation of a cyclized structure. Marvel and co-workers [5, 6] showed that the heating of both these polymers produced cyclized and crosslinked units (II and III), where R is H and CH₃) through intra- and intermolecular condensation, respectively:



From Fig. 1, it is also observed that the temperatures of the beginning of weight loss increase in the order: poly(MIPK) < poly(MVK) < poly(EVK) < poly(IPVK) < poly(t-BVK) < poly(PVK), and with this order the subsequent weight loss also increases rapidly. Therefore, the thermal stability of the RVK polymers obtained by AIBN seems to increase in the above order.

This order is also supported by DTG curves for the copolymers of RVK with styrene (St), as is shown in Fig. 2. In Fig. 2, the maxima of the curves, i.e., the temperatures at the maximum rates of weight loss, are found to be 397°C for copoly(t-BVK/St) and 385-378°C for the other RVK copolymers.

Such a tendency in the thermal stability is also supported by the results of thermal degradation of the RVK copolymers with styrene at 210°C. In these cases, the samples used were copolymers of RVK with styrene in order to prevent gelation during the reaction. Figure 3 shows the IR spectra observed before and after thermal degradation of the copoly(MVK/St) at 210°C for 6 hr under a nitrogen atmosphere. After thermal degradation, a new peak is observed at around 1650 cm⁻¹, which seems to correspond to the C=C group in cyclohexenone ring [7], which shows the formation of the structure II.

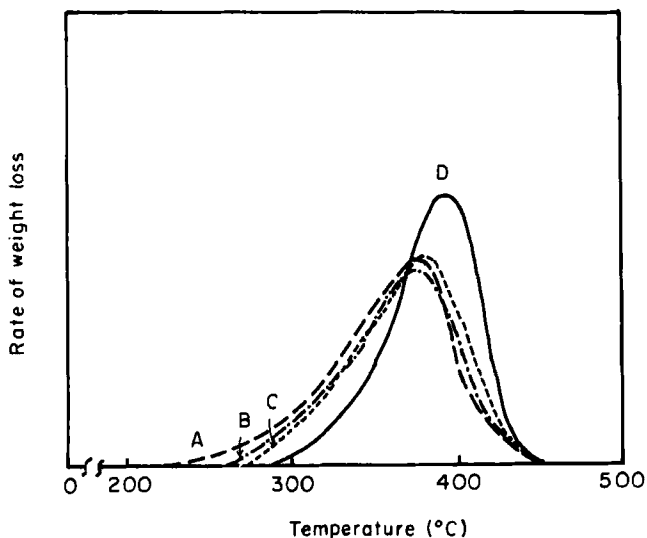


FIG. 2. Derivative thermogravimetric curves of the copolymers of RVK with styrene: (A) copoly(MVK/St); (B) copoly(EVK/St); (C) copoly(IPVK/St); (D) copoly(t-BVK/St).

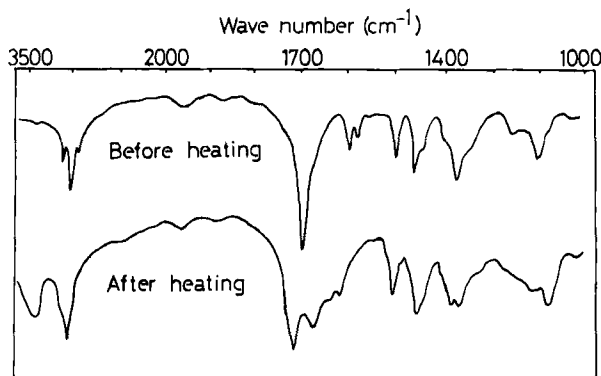


FIG. 3. Infrared spectra of the copoly(MVK/St) before and after heating for 6 hr at 210°C under a nitrogen atmosphere; molar ratio MVK/St = 50/50.

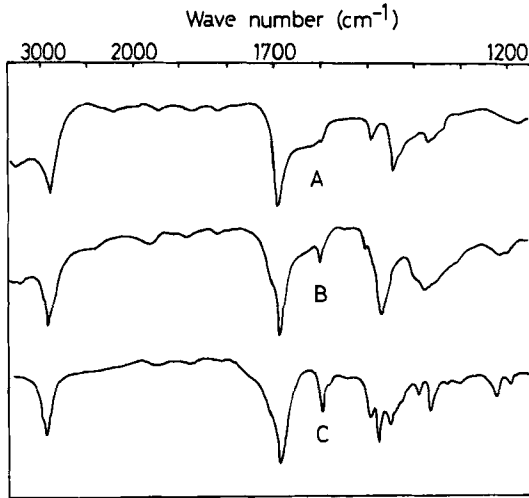


FIG. 4. Infrared spectra of the copoly(RVK/St) heated for 6 hr at 210°C under a nitrogen atmosphere; molar ratio RVK/St = 50/50.

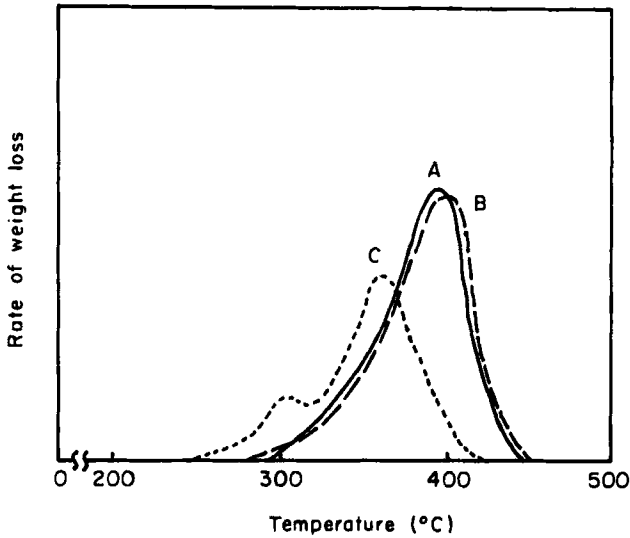


FIG. 5. Derivative thermogravimetric curves of polymers: (A) poly(*t*-BVK); (B) poly(St); (C) poly(methyl methacrylate).

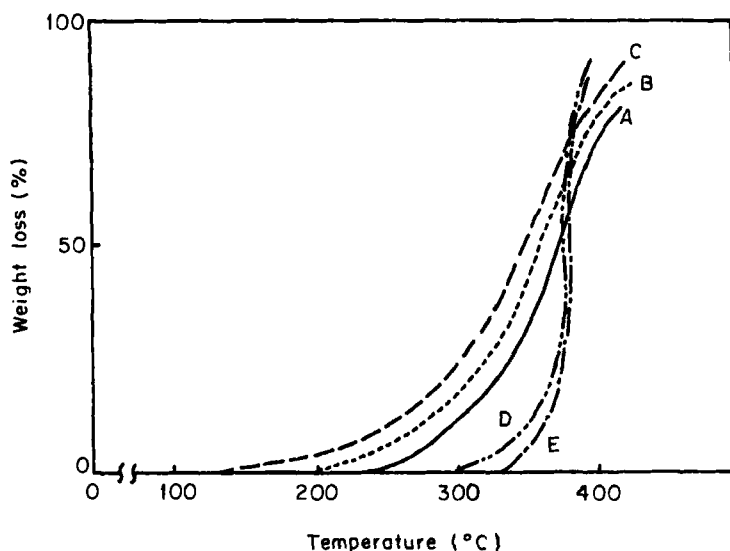


FIG. 6. Thermogravimetric curves of the poly(RVK): (A) poly(MVK) obtained with AIBN; (B) poly(MVK) obtained with $\text{Al}(\text{i-Bu})_3$ and BuLi; (C) poly(MVK) obtained with $t\text{-BuOK}$ in the presence of $N\text{-phenyl-}\beta\text{-naphthylamine}$; (D) poly($t\text{-BVK}$) obtained with AIBN; (E) poly($t\text{-BVK}$) obtained with various anionic initiators (see Table 1).

On the other hand, there is no change in the IR spectrum of poly($t\text{-BVK}$) under similar conditions, as is shown in Fig. 4c. From this figure, it might be concluded that the degree of such cyclization was influenced by alkyl substituents in RVK copolymers, decreasing in the order: copoly(MVK/St) > copoly(EVK/St) > copoly(IPVK/St) > copoly($t\text{-BVK}$ /St).

To compare the thermal stability of the RVK polymers such as poly($t\text{-BVK}$) with the other polymers such as polystyrene and poly(methyl methacrylate), DTG curves were recorded. The results are represented in Fig. 5, from which the thermal stability of poly($t\text{-BVK}$) seemed to be more similar to that of polystyrene rather than that of poly(methyl methacrylate).

As mentioned above, $t\text{-BVK}$ polymer and copolymer with styrene were found to be comparatively stable to heating. Such stability of this polymer seems to depend not only on no reactive hydrogen atom of tert-butyl group, but also on the bulkiness of its group.

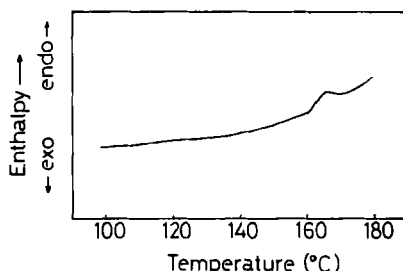


FIG. 7. Differential scanning calorimetric curve of poly(*t*-BVK) obtained with anionic initiator (10°C/min under nitrogen).

Thermal Stability of Anionically Obtained Polymers

In contrast to the polymers obtained by AIBN, TG curves of the anionically obtained RVK polymers vary according to the substituents, as shown in Fig. 6. For example, the temperature of the beginning of weight loss for poly(MVK) obtained by *t*-BuOK is lower than that of poly(MVK) obtained with AIBN, which is contrary to the case of poly(*t*-BVK). One of the reasons seems to be the low molecular weight of the former ($\bar{M}_n = 1500\text{--}3100$ by GPC). However, the polymer of *t*-BVK obtained by radical polymerization is slightly less stable than that of polymer obtained by anionic polymerization, probably because of the isotactic structure of the latter.

Figure 7 shows the DSC curve of the anionically obtained isotactic poly(*t*-BVK). At 160–170°C, an endothermic peak is observed. Therefore, the glass transition temperature of this polymer was determined to be about 160°C. This value is higher than those of polystyrene (100–105°C) and poly(methyl methacrylate) (72–105°C).

REFERENCES

- [1] C. S. Marvel and C. L. Levesque, J. Amer. Chem. Soc., **60**, 280 (1938).
- [2] C. S. Marvel, E. H. Riddle, and J. O. Corner, J. Amer. Chem. Soc., **64**, 92 (1942).
- [3] N. Grassie and J. N. Hay, Makromol. Chem., **64**, 82 (1963).
- [4] J. N. Hay, Makromol. Chem., **67**, 31 (1963).

- [5] K. Matsuzaki and J. C. Lay, Makromol. Chem., 110, 185 (1967).
- [6] I. C. McNeil and D. Neil, Eur. Polym. J., 7, 115 (1971).
- [7] K. Matsuzaki and S. Ohshima, Makromol. Chem., 164, 265 (1973).
- [8] T. Otsu and H. Tanaka, J. Polym. Sci. Polym. Chem. Ed., 13, 2065 (1975).
- [9] H. Tanaka and T. Otsu, J. Macromol. Sci.-Chem., A11, 231 (1977).
- [10] H. Tanaka and T. Otsu, J. Polymer Sci. Polym. Chem. Ed., in press.

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