

THE WAVELENGTH DEPENDENCE OF THE PHOTODEGRADATION OF THE HOMOPOLYMER AND COPOLYMERS OF 2-METHYL-1-PHENYL-2-PROPEN-1-ONE

IKUO NAITO, KAZUO TASHIRO and AKIHIRO KINOSHITA

Department of Photography, Kyushu Sangyo University, Fukuoka (Japan)

WOLFRAM SCHNABEL

Bereich Strahlenchemie, Hahn-Meitner-Institut für Kernforschung Berlin G.m.b.H., D-1000 Berlin 39 (F.R.G.)

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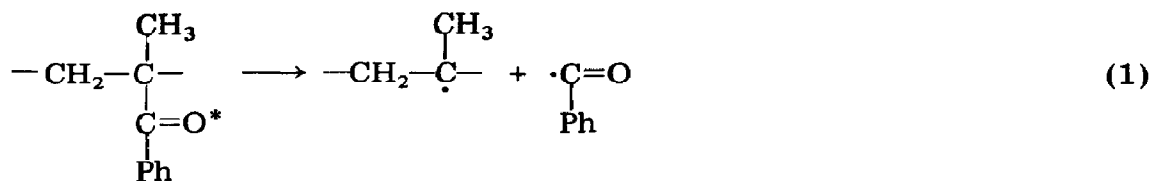
Summary

The photodegradations of the homopolymer of 2-methyl-1-phenyl-2-propen-1-one and of its copolymers with styrene and methyl methacrylate were studied by continuous irradiation of dioxane solutions at $\lambda = 254$ nm. Significantly higher quantum yields of the homopolymer were found at this wavelength than at 313 nm (values given in parentheses): $\phi(S) = 0.17$ (0.05), $\phi(\text{benzaldehyde}) = 0.7$ (0.3) and $\phi(\text{monomer}) = 2.0$ (0.5) ($\phi(S)$ is the quantum yield of main-chain scission). Similar results were obtained for the copolymers. Flash photolysis of the homopolymer in CH_2Cl_2 solution at 265 nm showed that both triplets and benzoyl radicals were formed during the 15 ns flash. However, at 347 nm only triplets were detected at the end of the flash. It is therefore concluded that, after excitation to the S_1 state at $\lambda > 300$ nm, photolysis proceeds mainly via the lowest triplet state T_1 which is relatively stable and is only partly deactivated via the chemical route of bond scission. On excitation to the S_2 state at $\lambda = 254$ nm, the probability of bond scission is significantly higher. These results suggest that α scission occurs from the S_2 state in competition with intersystem crossing to T_n and that the rate constant of the latter process is lower than that of the former.

1. Introduction

Earlier studies [1, 2] of the photolysis of poly(2-methyl-1-phenyl-2-propen-1-one), which is also known as poly(phenyl isopropenyl ketone) (PIIK), at $\lambda > 300$ nm have revealed the following.

(a) In the homopolymer α cleavage (type I process) according to the reaction

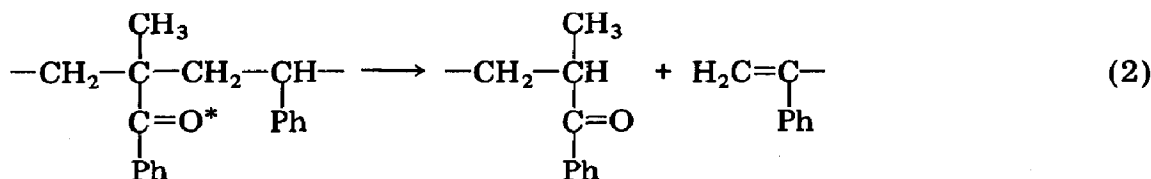


is the dominant primary photolytic process.

(b) The lowest excited triplet state n,π^* acts as the precursor to bond cleavage.

(c) The triplet lifetime and the quantum yield $\phi(S)$ of the main-chain scission of copolymers of phenyl isopropenyl ketone (PIK) and methyl methacrylate (MMA) are independent of copolymer composition indicating that the photolysis of the PIK moieties is not notably influenced by the neighbouring MMA units.

(d) Copolymers of PIK and styrene (St) undergo β cleavage (type II process) according to



The extent of this process increases with decreasing PIK content, *i.e.* with increasing probability of the PIK moieties having styrene units as nearest neighbours.

The aim of this paper was to investigate the influence of the wavelength of the incident light on the photolysis of PPIK and of copolymers of PIK with MMA and St. For this purpose continuous and flash irradiations of dilute polymer solutions were carried out at 254 nm and 265 nm respectively. The species under investigation were excited to a higher electronic level at these wavelengths than at the wavelengths of 313 and 347 nm used in earlier work [1, 2]. This is shown in Fig. 1 where the absorption spectrum of PPIK in dioxane solution is presented.

As described below, higher quantum yields for main-chain scission and for the formation of benzaldehyde, which was the main product of the photolysis, were found for both the homopolymer and the copolymers on irradiation at lower wavelengths. A real wavelength dependence of photochemical reactions in saturated ketones has been observed in only a few cases, as has been pointed out in a review article by Turro *et al.* [3].

2. Experimental details

2.1. Materials

PIK was synthesized from propiophenone and paraformaldehyde via a Mannich reaction and was polymerized anionically in dioxane solution. The

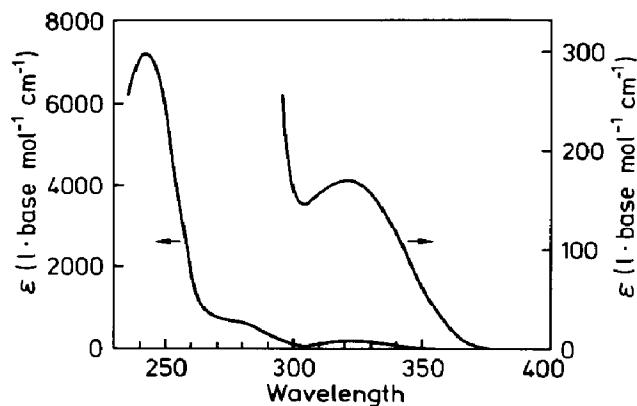


Fig. 1. Optical absorption spectrum of PPIK in dioxane solution.

TABLE 1

Characterization of polymer samples

<i>Polymer</i>	<i>PIK content (mol.%)</i>	<i>Weight average molecular weight</i>
PPIK	100	6×10^3 ^a
CP-PIK-St-19	18.5	4×10^4
CP-PIK-St-10	10.1	5×10^4
CP-PIK-St-7	7.0	7×10^4
CP-PIK-St-6	5.7	8×10^4
CP-PIK-St-2	1.8	1.8×10^5
CP-PIK-MMA-19	18.8	6×10^4
CP-PIK-MMA-12	11.7	1.2×10^5
CP-PIK-MMA-9	8.6	1.7×10^5
CP-PIK-MMA-7	6.8	2.6×10^5
CP-PIK-MMA-3	2.6	9.3×10^5

^aNumber average molecular weight.

copolymers were synthesized by thermally initiated free-radical emulsion polymerization (5 h at 80 °C). Sodium *p*-dodecylbenzene sulphonate and sodium oleate were used as the emulsifiers. The polymers were reprecipitated three times from benzene solution with methanol. All the polymer samples used in this work are listed in Table 1.

2.2. Determination of the molecular weight

The number average molecular weight (MW) of PPIK was determined by vapour pressure measurements using a Hitachi-Perkin-Elmer model 115 apparatus. The weight average MWs of the copolymer samples CP-PIK-St-19 and CP-PIK-MMA-19 were determined by gel permeation chromatography based on calibration with standard polystyrene samples. In all other cases the

MW was estimated from the intrinsic viscosity using the following $[\eta]$ -molar mass M relations reported in the literature: $[\eta] = 9.52 \times 10^{-5} M^{0.74}$ (polystyrene in benzene at 25 °C) [4] and $[\eta] = 6.27 \times 10^{-5} M^{0.76}$ (poly(methyl methacrylate) in benzene at 30 °C) [5].

2.3. Determination of benzaldehyde and monomer

After irradiation the polymer was precipitated by adding methanol to the sample solution. The two molecular reaction products remained in the liquid phase and were determined by gas chromatography using a Shimadzu type 5A apparatus which incorporated a 2 m PEG 20M column ($T = 150$ °C). Acetophenone was used as the standard.

2.4. Continuous irradiation

The degassed solutions of the polymers in dioxane were irradiated at 30 °C in quartz ampoules using a 10 W low pressure mercury lamp. Filters were not used. The output of the 253.7 nm line was about 100 times greater than that of all the other lines in the wavelength range up to $\lambda = 350$ nm corresponding to the high wavelength absorption band of the polymers (see Fig. 1). As the absorptivity is rather low, the contribution of the absorbed dose accumulated at $\lambda > 253$ nm relative to the dose absorbed by the polymers at $\lambda = 253.7$ nm is negligibly small.

Actinometry at 253.7 nm was accomplished with the aid of tetraphenylcyclobutane using the cycloreversion reaction in acetonitrile. The quantum yield for *trans*-stilbene formation was redetermined as 0.68, which is at variance with values published earlier (0.84 [6] and 0.27 [7]).

2.5. Laser flash photolysis

The light source was a neodymium-doped yttrium aluminium garnet laser (J. K. Lasers Ltd.) with a glass amplifier (Korad). The 1060 nm light was frequency quadrupled using potassium dideutero phosphate and ammonium dihydrogen phosphate crystals.

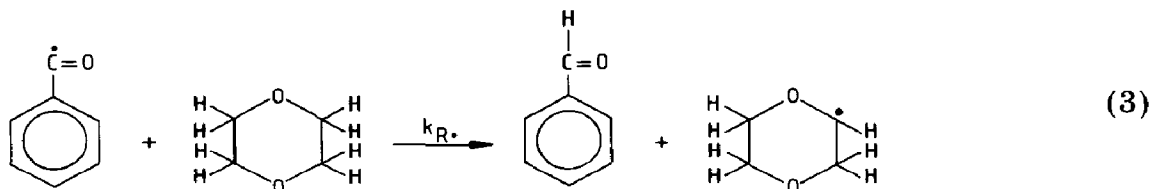
Actinometry for the 265 nm light was accomplished with the aid of tetraphenylcyclobutane ($\phi(\text{stilbene}) = 0.68$). Single 15 ns flashes were used to irradiate solutions of PPIK in dichloromethane at a concentration of 0.024 g l^{-1} at 20 °C. The samples were contained in rectangular quartz cells. The typical absorbed dose per flash was $2 \times 10^{-5} \text{ einstein l}^{-1}$.

3. Results

3.1. Continuous irradiation

3.1.1. Formation of benzaldehyde

If α cleavage occurs according to reaction (1), benzoyl radicals are formed. In dioxane solution most of these radicals react with the solvent via hydrogen abstraction:



Reactions between two benzoyl radicals, or between benzoyl radicals and macroradicals, are very improbable because of the low stationary radical concentration. Hydrogen abstractions by benzoyl radicals from the polymer are possible in principle, but they are not important in this case because the rate constants for hydrogen abstraction are about the same for both the polymer and the solvent, and the concentration of the latter is much higher than that of the former ($k_R[\text{dioxane}] \gg k_R[\text{polymer}]$).

Figure 2(a) shows plots of the formation of benzaldehyde during the photolysis of PPIK and of the copolymers CP-PIK-St-19 and CP-PIK-MMA-12 as a function of the dose absorbed by the polymer. For comparison, data obtained during the photolysis at 313 nm are presented in Fig. 2(b). Quantum yields estimated from the initial slopes of the curves are given in Table 2. In the case of the homopolymer benzaldehyde is generated with a quantum yield of about 0.7. The yields from the copolymers are lower, particularly for CP-PIK-St-19. In all cases the quantum yields at 254 nm are about twice those at 313 nm.

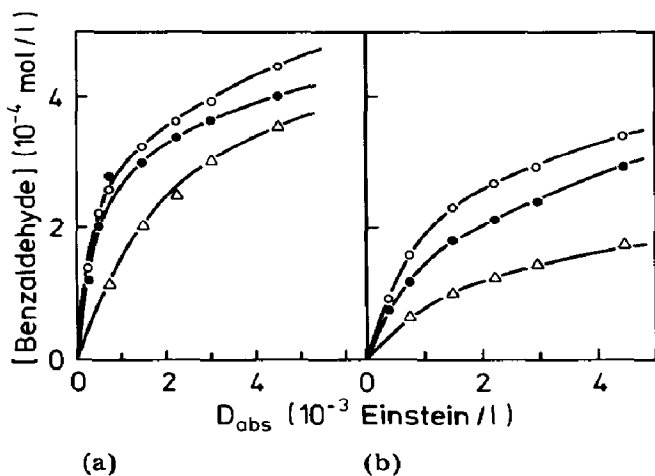


Fig. 2. Formation of benzaldehyde during the continuous irradiation of PPIK and copolymers of PIK in degassed dioxane solutions at 30 °C and (a) 254 nm or (b) 313 nm as a function of the absorbed dose (polymer concentration, 5 g l⁻¹): ○, PPIK; △, CP-PIK-St-19; ●, CP-PIK-MMA-12.

3.1.2. Main-chain scission

The number α_s of scissions per initial macromolecule is plotted against the absorbed dose for the homopolymer PPIK in Fig. 3. Again, α_s is significantly higher at 254 nm than at 313 nm. Quantum yields are given in

TABLE 2

Photolysis of the homopolymer and the copolymers of 2-methyl-1-phenyl-2-propen-1-one in dioxane solution (continuous irradiation at 254 and 313 nm)

Polymer	$\phi(S)^a$		$\phi(\text{benzaldehyde})$		$\phi(\text{monomer})$	
	254 nm	313 nm	254 nm	313 nm ^b	254 nm	313 nm
PPIK	0.17	0.05	0.7 ± 0.1	0.30 ± 0.05	2.0 ± 0.4	0.5 ± 0.1
CP-PIK-St-19	0.12	0.06	0.20 ± 0.05	0.10 ± 0.03	—	—
CP-PIK-MMA-12	0.12	0.04	0.50 ± 0.10	0.20 ± 0.05	—	—

^aNumber of main-chain scissions per photon absorbed by the polymer.

^bDetermined in benzene solution containing pentane-1-thiol (0.5 mol l^{-1}).

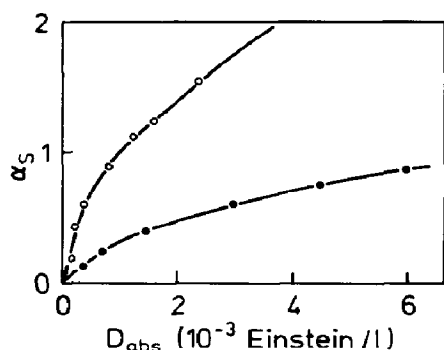


Fig. 3. The number α_S of scissions per initial macromolecule during the continuous irradiation of PPIK in degassed dioxane solution at 30°C as a function of the absorbed dose (polymer concentration, 5 g l^{-1} ; $\alpha_S = \overline{DP}_0/\overline{DP}_D - 1$, where \overline{DP}_0 and \overline{DP}_D are the degrees of polymerization before and after irradiation respectively); \circ , $\lambda = 254 \text{ nm}$; \bullet , $\lambda = 313 \text{ nm}$.

Table 2. The following observations were made for the copolymers of PIK and St. In deaerated dioxane solution polystyrene was barely degraded on irradiation at 254 nm and was unaffected at $\lambda > 300 \text{ nm}$. Incorporation of PIK moieties into polystyrene led to a substantial increase in $\phi(S)$. This is probably due to the fact that, because of the statistical distribution of the monomer units in the polymer chains, most PIK units are isolated at low PIK content. Main-chain scission via β scission (Norrish type II process) is therefore possible.

It was found that $\phi(S)$ increased with increasing PIK content and approached the $\phi(S)$ value of the homopolymer PPIK. This indicates that the energy absorbed by the St units at 254 nm sensitized the main-chain scission. This effect was not observed at 313 nm where the St units do not absorb light. In contrast, $\phi(S)$ appeared to decrease somewhat with increasing PIK content.

$\phi(S)$ for the copolymers with methyl methacrylate did not depend on the copolymer composition. Poly(methyl methacrylate) underwent main-chain scission in deaerated dioxane solution at 254 nm with $\phi(S) = 3 \times 10^{-2}$. Copolymers containing between 3 and 19 mol.% PIK underwent main-chain

scission with $\phi(S) = 0.12$. The scission yield $\phi(S) = 4 \times 10^{-2}$ at 313 nm was independent of the copolymer composition. This result is as expected because γ hydrogen atoms, which are pre-requisites for β scission, are not available in these copolymers.

3.1.3. Formation of monomer

Figure 4 shows the formation of the monomer as a function of the absorbed dose in the case of the homopolymer. Quantum yields corresponding to the initial slopes of the curves are given in Table 2. In agreement with the results reported above, the yield measured at 254 nm is higher than that obtained at 313 nm (2.0 compared with 0.5).

In both cases the monomer is formed by a short chain reaction (depolymerization) as is evident from the fact that the ratio $\phi(\text{monomer})/\phi(S)$ is about 10 at both 254 and 313 nm.

3.2. Laser flash photolysis

The transient spectrum shown in Fig. 5(a), curve 1, was generated during the irradiation of a PPIK solution in dichloromethane with a 15 ns flash of wavelength 265 nm. It decayed rapidly with a rate constant of $1.2 \times 10^7 \text{ s}^{-1}$ leaving the spectrum shown in Fig. 5(a), curve 2, which was very long lived ($k \leq 10^4 \text{ s}^{-1}$). The difference spectrum (Fig. 5(a), curve 3), which had maxima at $\lambda = 460 \text{ nm}$ and $\lambda \leq 300 \text{ nm}$, was obtained by subtracting spectrum 1 from spectrum 2 and was assigned to triplet states. It strongly

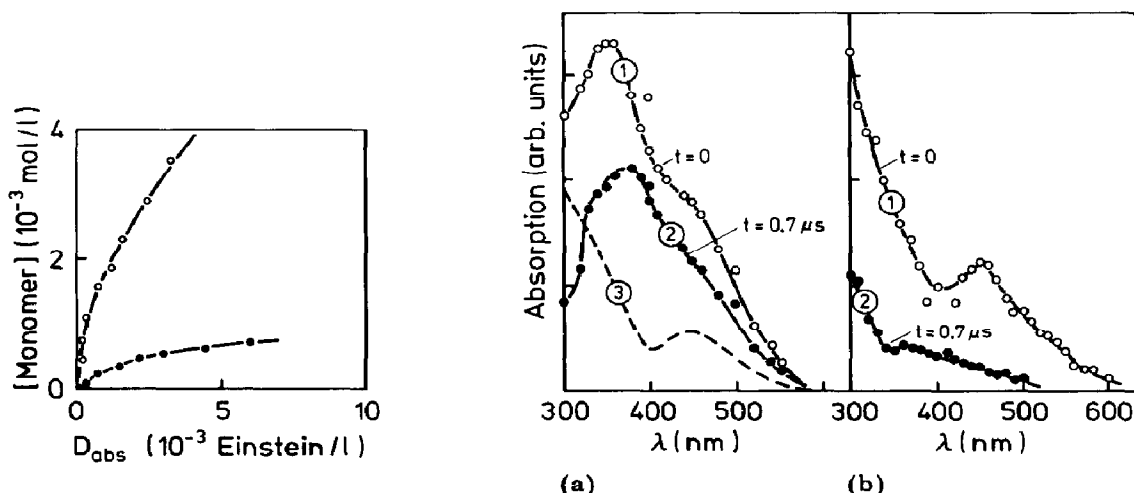


Fig. 4. Formation of PIK during the continuous irradiation of PPIK in deaerated dioxane solution at 30 °C and 254 nm (○) or 313 nm (●) as a function of the absorbed dose (polymer concentration, 5 g l^{-1}).

Fig. 5. Transient absorption spectra measured after the flash photolysis of PPIK in deaerated solutions at room temperature (curve 1, immediately after the flash; curve 2, $0.7 \mu\text{s}$ after the flash): (a) dichloromethane solvent, $[\text{PPIK}] = 2.4 \times 10^{-2} \text{ g l}^{-1}$, $\lambda = 265 \text{ nm}$ (curve 3, difference between curves 1 and 2); (b) benzene solvent, $[\text{PPIK}] = 2.2 \times 10^{-1} \text{ g l}^{-1}$, $\lambda = 347 \text{ nm}$.

resembles spectrum 1 in Fig. 5(b) which was generated during a 25 ns flash at 347 nm and was found [1] to decay with almost the same rate constant ($(1.0 \pm 0.1) \times 10^7 \text{ s}^{-1}$). The long-lived spectrum 2 in Fig. 5(a) with its maximum at 380 nm is ascribed to the benzoyl radical.

The spectrum formed during the 15 ns flash at 265 nm appears to be composed of at least two components, *i.e.* the triplet spectrum and the benzoyl radical spectrum. This contrasts with the observations made during the flash photolysis at 347 nm (see Fig. 5(b), curve 1). It can therefore be concluded that different mechanisms operate for excitation at $\lambda = 265 \text{ nm}$ and at $\lambda > 300 \text{ nm}$.

4. Discussion

The wavelength dependence of photochemical reactions has rarely been studied systematically to our knowledge. In connection with the work reported here, the investigations of Berger and coworkers [8, 9] are of greatest interest. These workers reported that the irradiation of acetophenone in the vapour phase resulted in α cleavage with $\phi < 10^{-2}$ when light was absorbed in the S_1 band. In contrast, $S_0 \rightarrow S_2$, S_3 excitation induced α cleavage with $\phi \approx 1.0$. Furthermore, cyclobutanones have been reported to undergo wavelength-dependent photochemical reactions in the gas phase [10, 11].

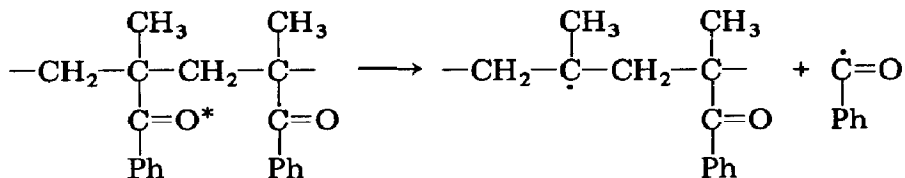
In investigations of photochemical reactions of cyclohexanones, Schaffner and coworkers [12] reported the existence of an interesting set of reactions occurring on excitation into the π, π^* absorption band at 254 nm which did not take place on excitation into the n, π^* absorption band by light of wavelength 313 nm or more (see the review by Schuster [13]). In some of these studies Schaffner and his colleagues concluded that the upper triplet states were populated and initiated chemical reactions.

Our results clearly indicate that the excited carbonyl groups in PPIK were deactivated almost entirely via the chemical route of α scission if excitation occurred via an $S_0 \rightarrow S_2$ process. This is inferred from the high quantum yield for benzaldehyde at 254 nm (0.70 ± 0.1). The results do not allow a definite conclusion as to whether α scission occurs from an S_2 state or from a higher triplet (T_n) state. The flash photolysis studies at 265 nm showed that a small fraction of the excited chromophores temporarily exist in the lowest excited triplet state T_1 . A major pathway $S_0 \rightarrow S_2 \rightarrow T_n \rightarrow T_1$ for α scission can be excluded, however, because excitation of T_1 via $S_0 \rightarrow S_1 \rightarrow T_1$ during irradiation of PPIK with light of wavelength greater than 300 nm resulted in relatively low quantum yields for benzaldehyde formation. At present we are inclined to assume that α scission and intersystem crossing from S_2 are competing ($k_{4b} > k_{4a}$):

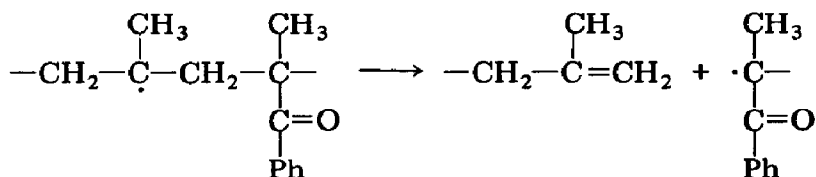


(4b)

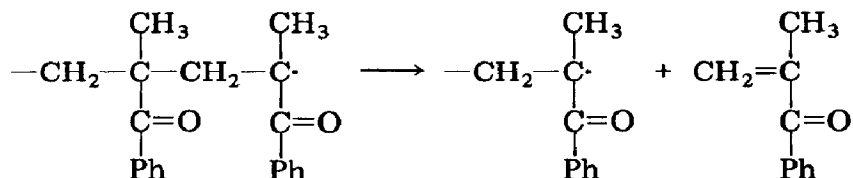
The important chemical reactions ensuing from excitation of PPIK are depicted in the following scheme: (a) α cleavage



(b) main-chain scission via β cleavage



(c) depolymerization



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