Plasma-Induced Polymerization

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Synopsis

Low vapor tension polymerized acrylates as thin films when they are subjected to a cold plasma. The plasma-induced polymerization is described in terms of direct or indirect energy transfer from the plasma to the monomer. The indirect transfer is related to the absorption of UV-visible radiations by the monomer. The radiations are emitted from excited species of the plasma. Direct transfers correspond to the reactive species collision (radicals, ions, metastable species) with a molecule of monomer. The polymerization is a result of these two kinds of transfers. Direct transfers lead to competitive reactions (addition, terminations and degradation, etc.) and acrylate polymerization is mostly induced by the UV-visible radiations.

INTRODUCTION

Previous investigations deal with plasma polymerization or polymer modification.[1] One example of plasma polymerization is generally called plasma-induced polymerization: in this case, the plasma initiates the polymerization at the surface of liquid or solid monomers.[2,3] Multifunctional acrylates, such as trimethylolpropane triacrylate (TMPTA) and polyethyleneglycol diacrylate (PEGDA), can be polymerized via this route. The plasma-induced polymerization of these monomers has been described as a function of several parameters (chemical structure of the monomer, film thickness, gas nature, pressure, discharge power, polymerization with or without initiator, coinitiator, etc.).[4-7]

Clark et al.[8,9] have introduced the concept of direct or indirect energy transfer for cold plasma modification of polymers. The indirect transfer corresponds to the UV-visible radiation absorption by the polymer and the direct one corresponds to the active species bombardment on the polymer surface. Following this concept, we attempt to describe the plasma-induced polymerization as a function of these two transfers.

EXPERIMENTAL

Monomers [trimethylolpropane triacrylate (TMPTA) and polyethyleneglycol diacrylate (PEGDA)] (Röhm and Hass) are used without further purification. They are spread with a Conway stick with a calibration of 6 μm on an aluminium foil which has been treated before under an O_2 plasma. Before the plasma-induced polymerization, the film is placed under vacuum for 15 min.
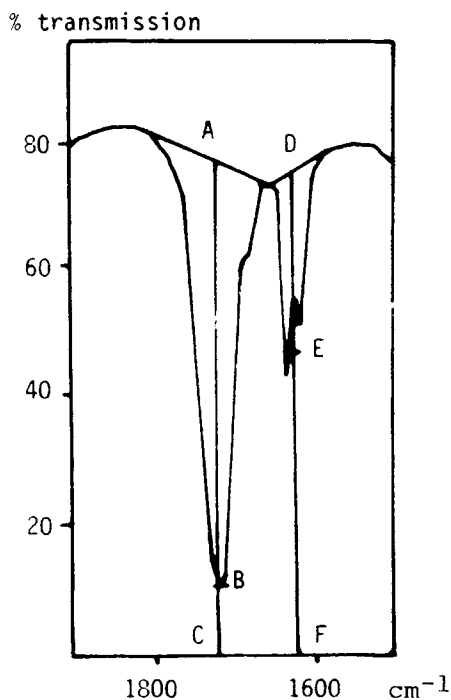
% transmission

Fig. 1. IR spectrum of TMPTA.

The plasma apparatus is a Brandson-IPC 4000 with a power generator operating at 13,56 MHz. The filter is a quartz quality glass transparent for $\lambda > 180$ nm.

The concentration of the residual double bonds $C{=}C$ (A) has been calculated as usual, from IR $C{=}C$ bands at 1640 cm^{-1} with $C{=}O$ absorption (1750 cm^{-1}) as reference. The $C{=}O$ and $C{=}C$ absorption are calculated on the polymer and monomer spectra (Fig. 1):

$$A_{C=O} = \ln(AC/BC) \implies A_{C=C}/A_{C=O})_{\text{polymer} + \text{monomer}} = \alpha$$
$$A_{C=C} = \ln(DF/EF) \qquad A_{C=C}/A_{C=O})_{\text{monomer}} = \beta$$

The conversion yield is assumed to be $(1 - \alpha/\beta) \times 100$ as the values of the absorption coefficients of the polymer and of the monomer are close together.

RESULTS AND DISCUSSION

Physical Aspects of the Plasma

The plasma is composed of several active species such as radicals, ions, free electrons, metastables, and excited species which, by falling down to their ground energy level, emit UV and visible radiations. These species have been identified and their concentration depend on plasma conditions (power, pressure, etc.).[10] The polymerization rate depends on the density of the excited

Fig. 2.   Diagram of the experimentation on the direct energy transfer induced polymerization.
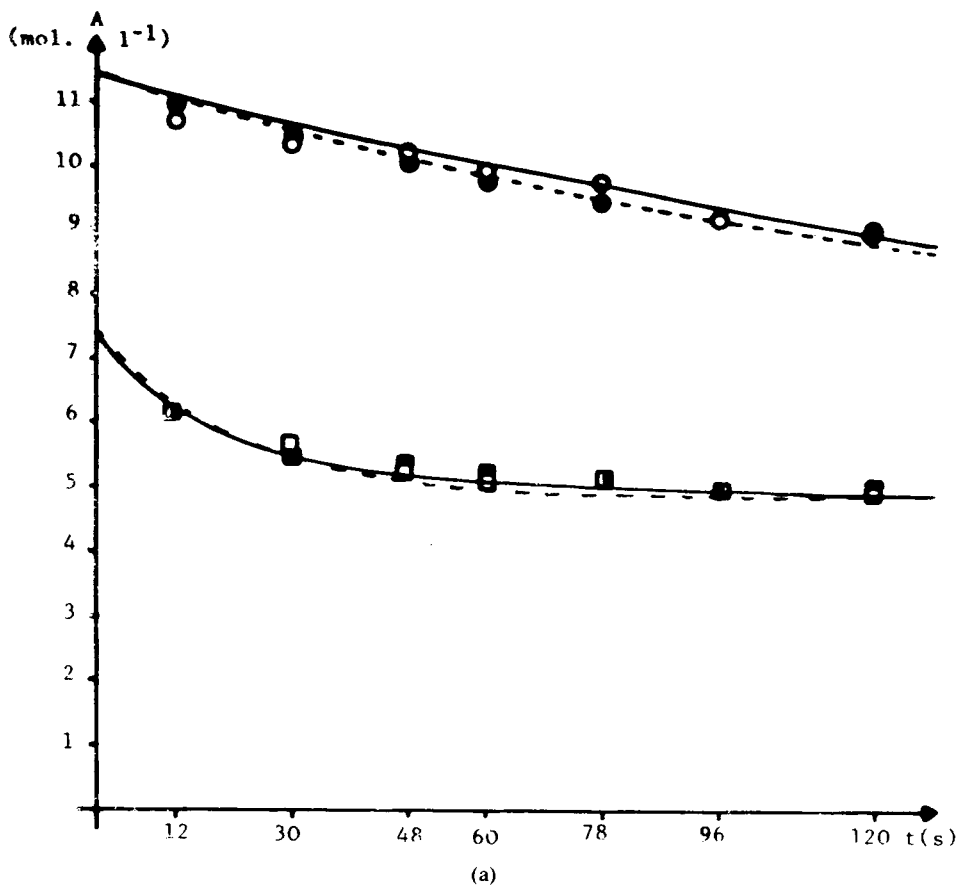

(a)

Fig. 3.   Plasma and direct energy transfer induced polymerization of TMPTA and PEGDA-200: (a) N_2 plasma; (b) He plasma; (c) CF_4 plasma. $D_{gas} = 100$ cm³/min STP, $P = 100$ W, $p = 0.56$ Torr, thickness of 6 μm. (-o-) TMPTA plasma; (- -•- -) TMPTA UV-visible radiations; (-□-) PEGDA plasma; (- -■- -) PEGDA UV-visible radiations.

species, as shown by the emission spectra recorded with or without monomer in the plasma.[10]

Kinetic Aspects of Plasma-Induced Polymerization

Therefore, more information on the influence of UV-visible radiations can be given. The initial polymerization rate $R_p)_{t=0}$ can be written following Clark's concept:

$$R_p)_{t=0} = R_p^\nu)_{t=0} + R_p^*)_{t=0}$$

with $R_p^\nu)_{t=0}$ the initial rate induced by the reactive species bombardment and $R_p^*)_{t=0}$ the initial rate induced by the UV-visible radiations absorption by the monomer.

The induced indirect transfer can be determined (Fig. 2) only by using quartz filter with different thickness (2, 4, and 6 mm). As a first approximation, one can assume that the polymerization rate is directly proportional to
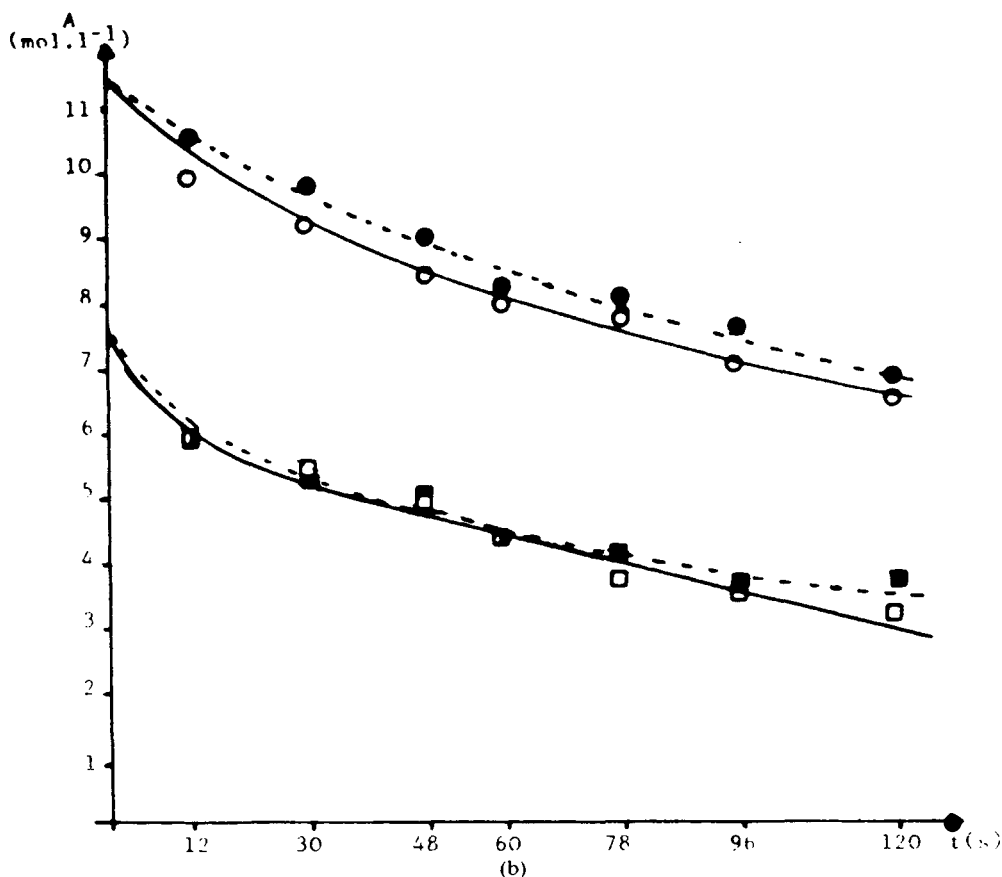

Fig. 3.   (Continued from the previous page.)

the radiation energy absorbed by the monomer

$$+ dx/dt = k \cdot (1 - x) \cdot E \qquad (1)$$

where x is the polymer yield and E the radiation energy absorbed by the monomer. E is the difference between the plasma energy and the energy dissipated or reflected by the filter. E is also a linear function of the filter thickness: $E = A - B \cdot l$ (A, B constants). Therefore, eq. (1) becomes

$$+ dx/dt = k(1 - x) \cdot (A - Bl)$$

$$\ln(1 - x) = A' + B' \cdot l \quad (A', B' \text{ constants}) \qquad (2)$$

By extrapolating the thickness to zero, the rate of polymerization induced by indirect energy transfer is obtained, which can be attributed to the polymerization rate induced by the UV-visible emission.
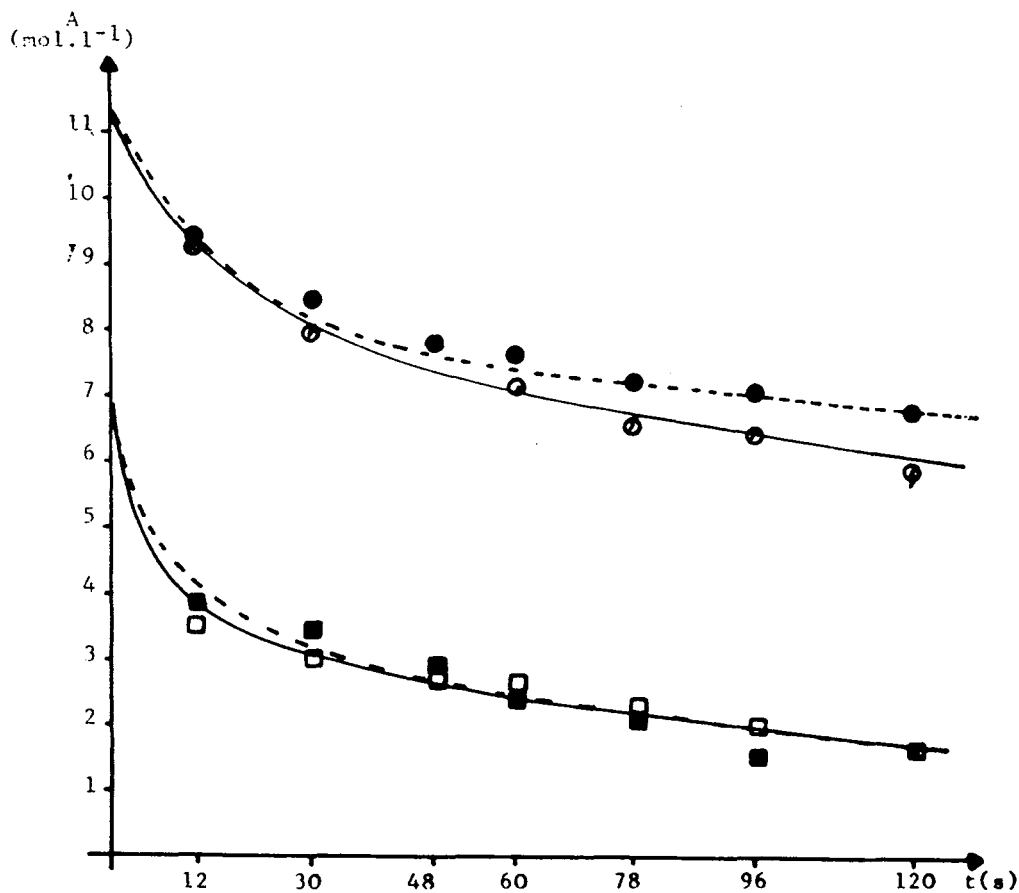

Fig. 3. (*Continued from the previous page.*)

Example of Polymerization Induced by Cold Plasma or Its Indirect Energy Transfer

The plasma-induced polymerization is studied in case of TMPTA and PEGDA. Helium, nitrogen, and tetrafluoromethane have been chosen as the plasma gases. The results are illustrated in Figure 3, where the data points corresponds to the experimental values of residual double bond concentration at a given time, whereas the curves illustrated theoretical kinetic diagrams. If the reactivity is equal for the three double bonds in the monomer, it varies during the polymerization due to the steric hindrance of the polymeric chains, as illustrated by the following scheme:
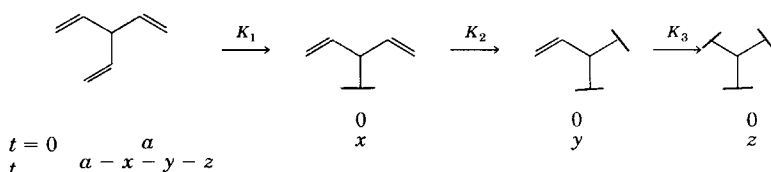
where a = monomer concentration, x = concentration of units having two residual double bonds, y = concentration of unit having one double bond, z = concentration of saturated monomer units, $K_1 > K_2 > K_3$,

$$+ dx/dt = 3K_1(a - x - y - z) - dy/dt - dz/dt$$

$$+ dy/dt = 2K_2(x) - dz/dt$$

$$+ dz/dt = K_3(y)$$

K_1, K_2, and K_3 are apparent constants as they include the radical concentration. The polymerization rate is first order with regard to the monomer concentration. $K_3(y)$ is negligible until the equations are applied to low polymerization yields. From the IR titration, only the total double bonds concentration dl is known:

$$dl = 3(a - x - y - z) + 2x + y$$

TABLE I
Rate Constants of PEGDA, TMPTA polymerization $(s^{-1}) \times 10^{+3}$ [a]

Monomer		Polymerization induced by UV-visible radiations			Polymerization induced by N_2 plasma
		He	CF_4	N_2	
TMPTA	K_1	6.43	20.73	2.93	2.43
	K_2	0.83	0.45	0.49	0.43
PEGDA	K_1	22.56	—	16.69	18.13
	K_2	0.36	—	16.69	16.13

[a] D_{gas} = 100 cm^3/min STP, P = 100 W, p = 0.56 Torr, film 6 μm.

A new expression of dl is obtained after integration of the differential equations:

$$\Rightarrow dl = 3a - \left[12K_1K_2a/(3K_1 + 2K_2)\right]t + \left[3K_1a/(3K_1 + 2K_2)\right]$$

$$\times \left\{\left[\left(4K_2/(3K_1 + 2K_2)\right)\right] - 1\right\}\left\{1 - \exp\left[-(3K_1 + 2K_2)t\right]\right\}$$

The equation obtained for diacrylate polymerization is simpler:

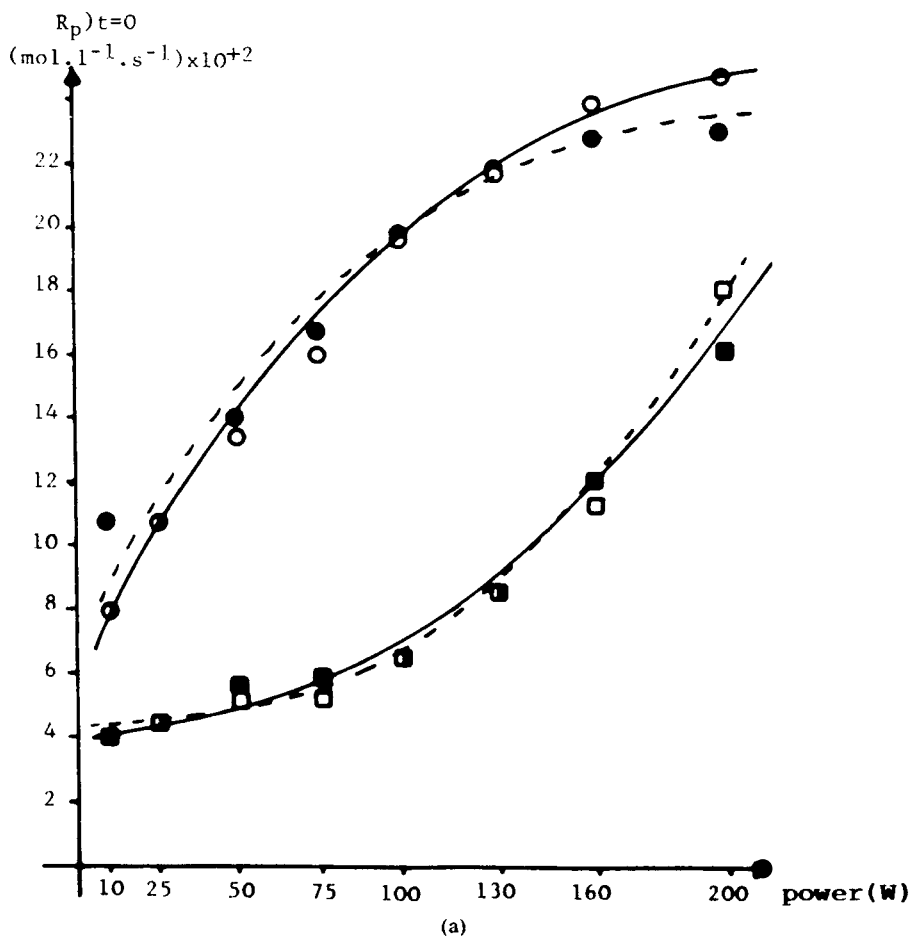$$dl = 2a - x = 2a - \left[2K_1a/(2K_1 + K_2)\right]\left\{1 - \exp\left[-(2K_1 + K_1)t\right]\right\}$$

Fig. 4. Dependence of PEGDA-200, TMPTA polymerization rate on discharge power. Plasmas: (a) N_2; (b) CF_4; (c) He. (-□-) TMPTA plasma; (- -■- -) TMPTA UV-visible; (-○-) PEGDA plasma; (- -●- -) PEGDA UV-visible. $D_{gas} = 100$ cm³/min STP, $P = 0.56$ Torr, film of 6 μm.

By the trial and error method with a microcomputer, it is possible to choose the pair (K_1, K_2) which gives the best curve fit to the experimental points. An iterative calculation beginning from a value of K_1 corresponding to a monomer with three totally independent double bonds has been used.

This calculation has been performed in the case of polymerization induced by the indirect energy transfer. In the chosen examples, no evidence of competition reactions have been noticed. For example, in case of nitrogen plasma induced polymerization, no evidence of surface modification has been noticed by ESCA (no oxidation or nitrogen bond). On the contrary, in He or
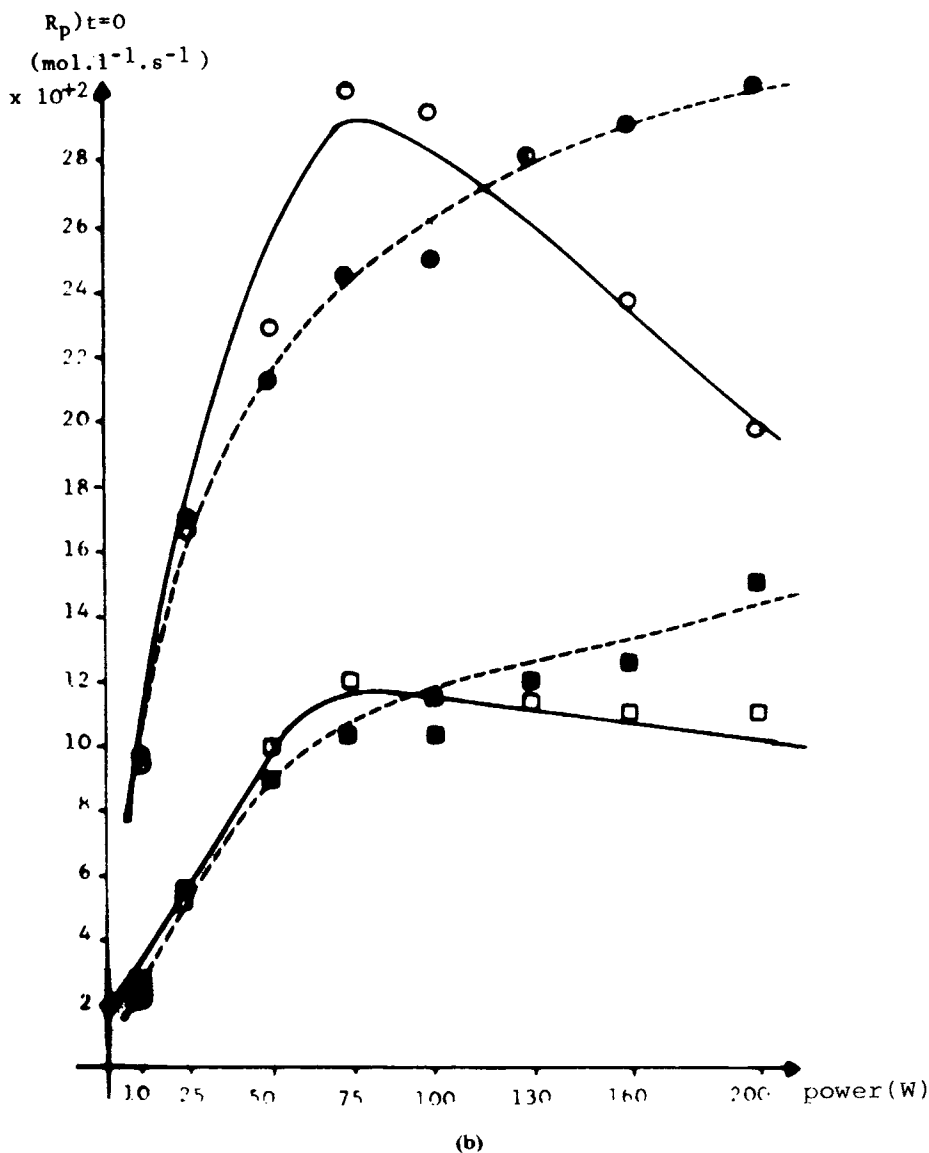

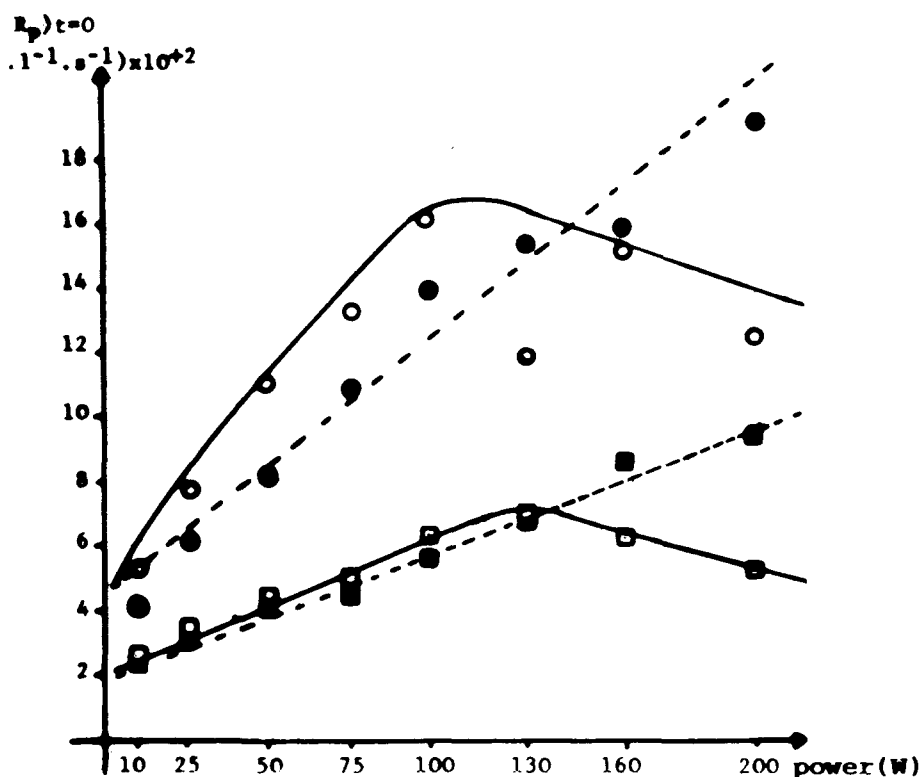Fig. 4.   (*Continued from the previous page.*)

CF_4 plasma induced polymerization the same kinetic schemes cannot be applied. More complexed schemes should be used.

The results are given in Figure 3. The indirect energy transfer seems to have the most important influence on the polymerization yield: Polymerization yields induced by nitrogen plasma or its UV radiations are similar. This results can be opposed to that of Johnson et al.,[11] who think that the radiations emitted by MMA plasma do not initiate the polymerization of this monomer. However, they do not take into account the radiation absorption due to the deposited PMMA. The different rate constants calculated from the proposed kinetic schemes are given in Table I.

Except in PEGDA polymerization induced by N_2 plasma or its radiations, K_2 is lower than K_1. The same results have been obtained at different powers.

Influence of Power on Polymerization and Initiation Rate Induced by the Cold Plasma or Its Radiation

A maximum rate depending on plasma parameter, has been noticed in surface modification or in the plasma polymerization of gaseous compounds.[1,11] An increase of one of these parameters does not lead to the studied effect but

(c)

Fig. 4.   (*Continued from the previous page.*)

TABLE II

Dependence of Rate Constants on Discharge Power in PEGDA-200 and TMPTA Polymerization[a]

			10	25	50	75	100	130	160	200
Power (W)										
UV plasma He	TMPTA	K_1	3.05	3.76	5.58	5.51	6.43	7.43	8.55	10.25
		K_2	0.05	0.06	0.05	0.28	0.83	1.43	1.23	0.24
	PEGDA	K_1	8.25	12.22	16.61	22.56	28.27	29.94	37.49	42.41
	200	K_2	7.25	3.11	1.51	0.36	2.27	0.94	1.49	3.26
UV plasma CF_4	TMPTA	K_1	1.66	7.78	13.34	16.67	20.73	23.74	31.36	38.16
		K_2	0.01	0.15	0.34	1.56	0.45	1.54	1.36	2.16
Plasma N_2	TMPTA	K_1	1.47	1.92	2.09	2.35	2.93	3.97	5.87	6.64
		K_2	0.28	0.29	0.10	1.15	0.49	1.65	0.43	2.64
	PEGDA	K_1	7.83	9.86	12.47	14.69	16.69	18.51	19.21	22.06
	200	K_2	7.83	9.86	12.47	14.69	16.69	18.51	17.21	17.04
UV plasma N_2	TMPTA	K_1	1.52	1.71	1.57	2.14	2.43	4.78	6.12	10.03
		K_2	0.28	0.31	0.12	1.14	0.13	0.78	0.87	1.43
	PEGDA	K_1	7.07	9.10	11.02	14.03	16.13	18.19	20.60	21.34
	200	K_2	7.07	9.10	11.02	14.03	16.13	18.19	16.20	15.34

[a]$(K_1, K_2 : s^{-1} \times 10^3.)$ $D_{gas} = 100$ cm^3/min STP, $P = 0.56$ Torr, film = 6 μm.
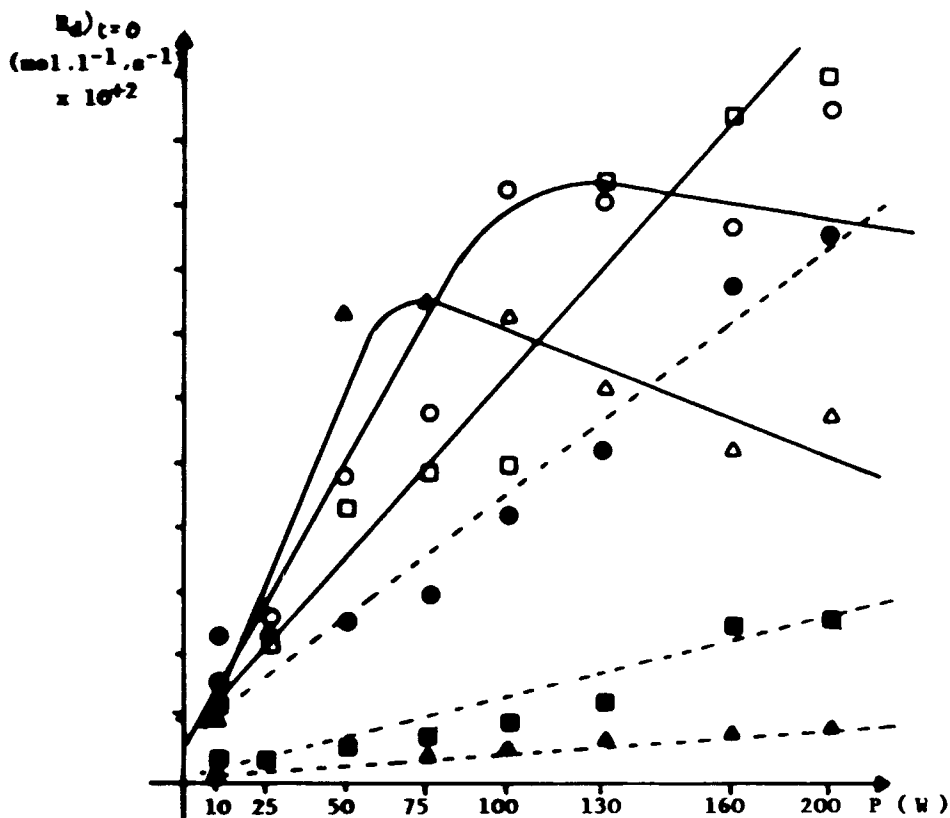
Fig. 5.   Dependence of PEGDA-200 initiation rate. $D_{gas} = 100$ cm^3/min STP, $p = 0.56$ Torr, film of 6 μm. (-□-) plasma N_2; (- - -■- - -) UV plasma N_2; (-○-) plasma He; (- - -●- - -) UV plasma He; (-△-) plasma CF_4; (- - -▲- - -) UV plasma CF_4.

sometimes to the opposite effect. Therefore, we have followed the incidence of the discharge power on the polymerization rate (Fig. 4).

In a nitrogen plasma, the two rates are similar and increase with the discharge power. In He or CF_4 plasma, the $R_p^v)_{t=0}$ increases with the power input; the increase is a linear function of power. The results confirm the direct relation between the density of excited species and the polymerization rate.[10] On the contrary, the global rates increase until a critical value of discharge power (75 W in CF_4 plasma, 130 W in He plasma) (Fig. 4) is reached. After this maximum, the polymerization rate decreased. These maxima in polymerization are significant of competitive reactions taking place during the polymerization. These reactions are probably degradation, addition, and termination, which become predominant at high power loadings. The IR analysis is not enough sensitive to get more information.

The rate constants K_1 and K_2 are given for different powers in case of the polymerization induced by radiations and by N_2 plasma in Table II. These rate constants increase with the discharge power; the effect is more important for K_1.

Initiation Step of Cold-Plasma-Induced Polymerization

Initiation rates are determined as described in Ref.[12] for PEGDA polymerization. The results (Fig. 5) can be compared to the polymerization rates: increase of polymerization induced by UV-visible emission and N_2 plasma polymerization, maximum in He, CF_4 plasma induced polymerization, respectively, at 130 and 75 W. But the ratio between the global rate and the rate induced by UV-visible radiations is higher for the initiation than for the polymerization. This effect may be assigned to a titration error due to the absorption of the UV-visible radiations by the diphenyl picryl hydrazile reagant which is used in this method. The competitive reactions (additions, terminations, degradations) are also observed in the initiation step of the polymerization.

CONCLUSION

The multifunctional acrylate polymerization induced by a cold plasma of helium, tetrafluoromethane, and nitrogen is described as a function of plasma parameters (discharge power, gas nature). In nitrogen plasma, the polymerization is mostly induced by UV-visible radiations emitted by the excited species present in the plasma. But, in He and CF_4 plasmas, competitive reactions to the polymerization are observed. Additions, terminations, and degradations lead to a decrease of the polymerization rate and they are predominant at a critical value of power depending on gas nature.

Further investigations will be carried out on the characterization of these competitive reactions; resulting products and the development of an analysis (UV-visible emission plasma spectroscopy) defining the interface between plasma and monomer-growing polymer will contribute to a best understanding of the plasma-induced polymerization and the excited species reactivity towards the monomer.

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