Effects and Role of the Solvents on the Plasma-Initiated Solution Polymerization of Vinyl Monomers[†]

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ABSTRACT: Plasma-initiated solution polymerization of vinyl monomers was carried out in various solvents. It was found that the polymerization took place exceedingly rapidly in the presence of water. It was also found that radicals generated from the plasma were efficiently trapped by solvated 2,2-diphenyl-1-picrylhydrazyl (DPPH), and from the rate of consumption of DPPH, the rate of radical liberation in the plasma was calculated as about $1 \times 10^{-5} \, \text{mol} \, l^{-1}$ per $1 \, \text{cm}^2$ of the diffusion area. A mechanism for the initiation process was envisioned in terms of the interaction between active species diffused from the gaseous plasma and liquid monomers. The possibility of solvation of ionic active species is proposed.
    KEY WORDS   Plasma / Plasma Polymerization / Plasma-Initiated Polymerization / Living Radical / Solvent Effect / 2-Hydroxyethyl Methacrylate / Poly(acrylamide) / Ultra-High Molecular Weight Polymer /

Recently Shen and coworkers reported a novel polymerization process whereby a low pressure cold plasma produced by an electric discharge is used to initiate the polymerization of liquid vinyl monomers.[1-3] This process is referred to as plasma-initiated polymerization and characterized by direct plasma exposure to liquid monomers as short as 60 sec of duration, followed by subsequent postpolymerization at room temperature or below. The resulting polymers are different from common plasma polymerized polymers, since they are uncrosslinked soluble polymers having extremely high molecular weights of $3 \times 10^7 \, \text{g} \, \text{mol}^{-1}$.[4] A kinetic study of the polymerization of methyl methacrylate (MMA) was carried out and showed that in the presence of plasma a monomer vapor is converted into a substance which later serves as an initiator for the polymerization of the liquid monomer. The tacticity distribution of the polymer[1,2] as well as the monomer–copolymer relationship[2,3] suggest that the polymerization is sustained by free radical propagation. However, some questions arise when the radical mechanism is simply assumed to account for the polymerization behavior:

1) Why is the polymerization so selective toward the monomer species?

n-Alkyl esters of methacrylic acid are polymerized by the plasma exposure, but no alkyl acrylates are susceptible to polymerization in bulk. Alkyl acrylates can be readily polymerized only when the monomer is emulsified with an appropriate amount of a surfactant in water.[5] Styrene (St), α-methylstyrene (α-MeSt), acrylonitrile (AN), *N*-vinylpyrrolidone (VPdn), sodium salt of *p*-styrenesulfonate (NaSS), and other vinyl monomers are not susceptible to the polymerization at present.

2) Why is the radical long-lived so as to induce postopolymerization, and how is it formed?

Once the monomer is exposed to the plasma, it can postpolymerize for a long period of time. It was found that the block copolymers were readily prepared using this initiation method.[6]

3) Why is the process of polymerization affected so strongly by solvents? What is the role of water on the polymerization?

It was previously reported that water soluble monomers such as acrylamide (AAM), acrylic acid (AA), methacrylic acid (MAA), and 2-hydroxyethyl

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methacrylate (HEMA) were polymerized very rapidly in water, but polymerized much more slowly in organic solvents such as DMF, DMSO, and ethanol. The ratio of the rates of polymerization in water and DMF was as large as 4000. As is well known the rate of radical polymerization is not significantly influenced by solvents in principle.

The present study was undertaken in an effort to shed some light on the mechanism of this unique polymerization method. Although final conclusions concerning the mechanism of the polymerization are not permissible at this point, there is evidence that electrons diffused from the gaseous plasma to the liquid monomer play an important role in the initiation process.

EXPERIMENTAL

The experimental apparatus and procedure used in this investigation were essentially the same as those described previously.[1,2,7-11] Liquid monomers and solvents were purified by vaccum distillation under argon. AAM, 2,2-diphenyl-1-picrylhydrazyl (DPPH), hydroquinone (HQ), and 2,2'-azobisisobutyronitrile (AIBN) were recrystallized from appropriate solvents.

Electric conductivity was measured in a specific cell with 10 mm × 10 mm platinum-platinum (black) electrodes 33 mm apart using a Shimadzu CM-30 at room temperature. Photo-polymerization was carried out by irradiation with a high-pressure mercury lamp (400 W) from distance of 50 cm throughout the polymerization.

RESULTS AND DISCUSSION

In a recent communication from our laboratory[6] we reported a specific acceleration effect of water on the rate of plasma-initiated polymerization of water soluble monomers. The resulting polymers were found to have very-high molecular weights and were successfully used to immobilize enzymes.[12] One great advantage of the immobilization with the aid of plasma-initiated polymerization is that it can readily be performed at low temperature and in a short plasma duration.

Figure 1 shows the effect of water concentration in DMF solution on the rate of polymerization of HEMA. It is seen that the rate of polymerization increases with an increasing water content, partic-
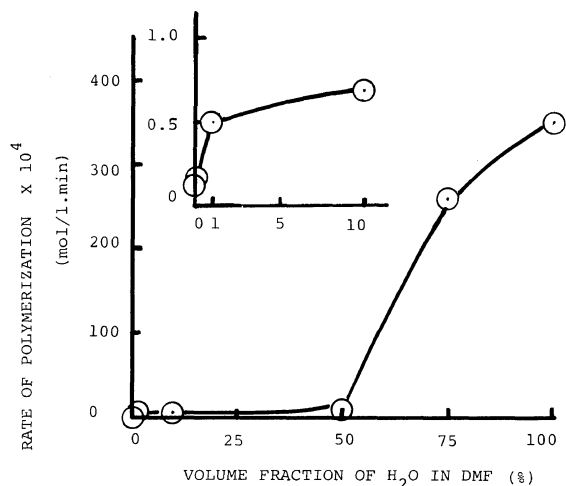

Figure 1. Effect of water concentration of the DMF solution on the rate of polymerization of 2-hydroxyethyl methacrylate (HEMA): HEMA, 4.15 mol l^{-1} (50 v/v%); plasma, 100 W, 60 s; postpolymerization, 25°C.

ularly when it exceeds 50 vol%. The rate of polymerization in water was calculated as 4300 times higher than that in DMF. The stong solvent effect observed here is quite unusual since no acceleration effect by water was observed in the photo- or chemically-initiated radical polymerizations of the same monomer.[6]

Figure 2 shows the dependence of the rate of polymerization on HEMA concentration in various solvent systems. A maximum was obtained at a monomer concentration of 50 v/v %, and both decreasing and increasing HEMA concentrations resulted in sharp drops of the polymerization rate. As is well established, the radical polymerization should increases the velocity in proportion to the monomer concentration. No such maximum was observed when the polymerization of HEMA was carried out by UV irradiation or by plasma exposure in organic solvents such as ethanol or DMSO, as shown in Figure 2.

We recently reported that plasma-exposed DMF is capable of initiating polymerization when vinyl monomers such as HEMA, AAM or MAA are subsequently mixed with the DMF.[13] However, no postpolymerization occurred when the monomer was mixed with plasma-exposed water. Quantitative "postreduction" was also observed when benzylviologen(1,1'-dibenzyl-4,4'-bipyridinium dichloride, BV^{2+}) or its polymer analogue, poly(xylylviologen
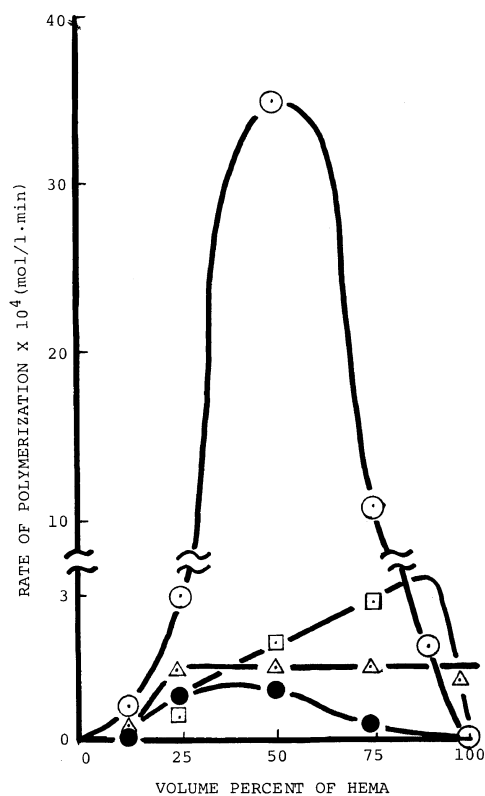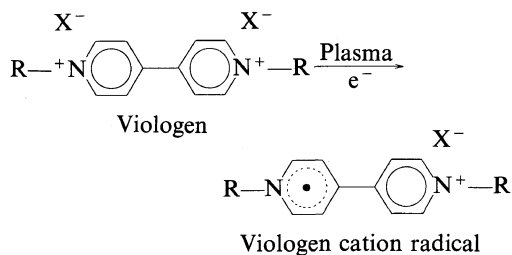
Figure 2. Monomer concentration dependence in various solvents on the rate of polymerization of 2-hydroxyethyl methacrylate (HEMA) by plasma ($\odot$, $\bullet$, $\boxdot$) and UV ($\triangle$) exposures. Plasma: 100 W, 60 s; postpolymerization, 25°C. UV: 400 W mercury lamp; in-source polymerization, 25°C. Solvent: $\odot$, $\triangle$, water; $\bullet$, ethanol; $\boxdot$, DMSO.

dichloride), was mixed with the plasma-exposed DMF. It was found that the viologens formed corresponding cation radicals according to the following equation[13]:

$$R—^+N\!\!\!\bigcirc\!\!\!-\!\!\!\bigcirc\!\!\!N^+—R \xrightarrow[e^-]{Plasma}$$

Viologen

$$R—N\!\!\!\overset{\cdot}{\bigcirc}\!\!\!-\!\!\!\bigcirc\!\!\!N^+—R$$

Viologen cation radical

R, Benzyl; X$^-$, Cl$^-$

$$d[BV^{\cdot+}]/dt = K[BV^{2+}]^{0.5}[\text{Plasma power}]^{1.0} \quad (1)$$

Table I. Plasma-initiated solution polymerization in various systems[a]

Plasma exposure	Added monomer	Conversion/%
Water	AAM	0
AAM		100
MAA		98
AAM + DMF		0.2
DMF	AAM	1.8
MAA + VPdn		1.7
MAA	VPdn	0
VPdn	MAA	9.0
AAM + BV		0.1
BV	AAM	0

[a] Monomer, 4 ml of 50 v/v% aqueous solution; benzylviologen, 10^{-3} mol l^{-1} DMF solution; water and DMF, 2 ml. Plasma, 13.56 MHz, 100 W, 60 s; postpolymerization, 25°C, 48 h.

where K is a constant dependent on the apparatus and condition. Here again, no reduction of viologen occurred by the plasma-exposed water. These experimental facts imply that the active species generated in DMF by the act of plasma are sufficiently long lived so as to induce "postpolymerization" or "postreduction." The stabilized active species in DMF should properly result in a lower activity of the polymerization, since the reactivity of active species is usually inversely-proportional to its life time. This assumption is consistent with the results shown in Figures 1 and 2. The available evidence also suggests that the active species responsible for the polymerization are produced by a direct action of electron–monomer reactions occurring in the gaseous plasma and liquid interface.

A variety of monomer solutions (or solvent) were initially exposed to the plasma for 60 s, and then a second monomer was subsequently mixed. The results of polymerization are summarized in Table I. It should be noted that water previously exposed to the plasma could not initiate the polymerization of monomer, although the monomers dissolved in it polymerized very rapidly as indicated before. This experimental result suggests that no long-lived active species responsible for the polymerization is formed in water. N-Vinylpyrrolidone (VPdn), which is a cyclic amide and sustains no polymerization itself by the plasma,
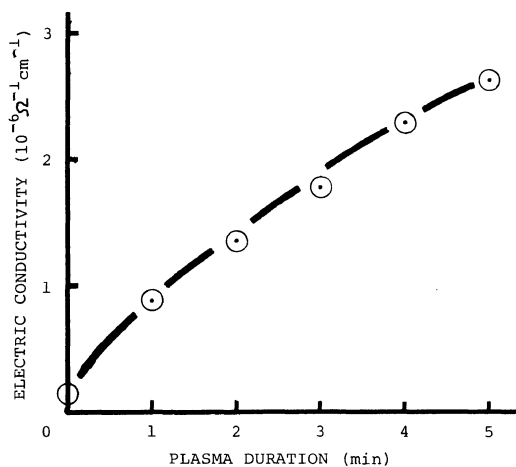
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Figure 3. Change in electric conductivity of DMF by plasma exposure: Plasma, 100 W.
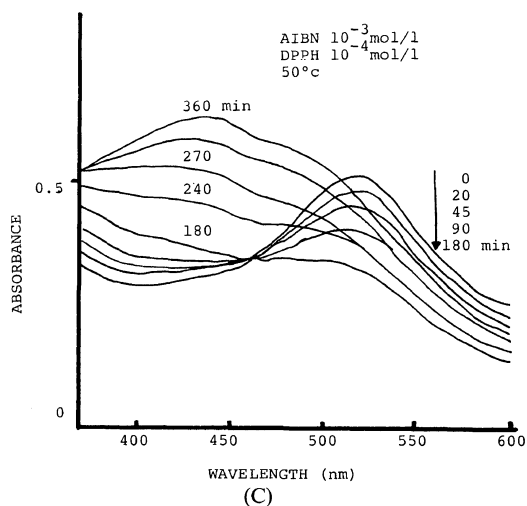

(A)

(B)

(C)

Figure 4. Progressive spectral changes of DPPH by plasma exposure (A, B) and thermal decomposition of AIBN (C) in DMF. Figures denote plasma duration (s) or AIBN decomposition time (min): Plasma, 100 W; DPPH, 10^{-4} mol l^{-1}; AIBN, 10^{-3} mol l^{-1}.
(A) The DMF solution of DPPH was exposed to plasma; (B) DMF was exposed to plasma, and then mixed with the DMF solution of DPPH; (C) AIBN was decomposed in the DMF solution of DPPH at 50°C.
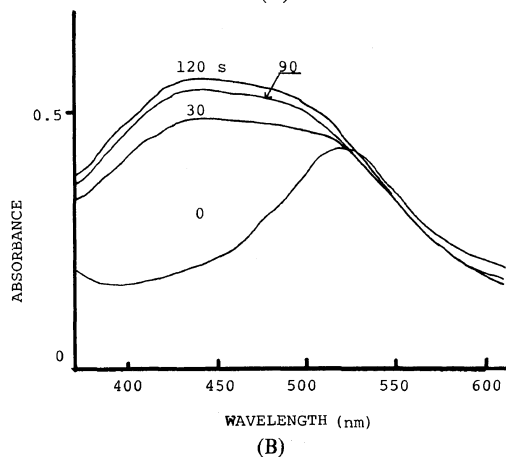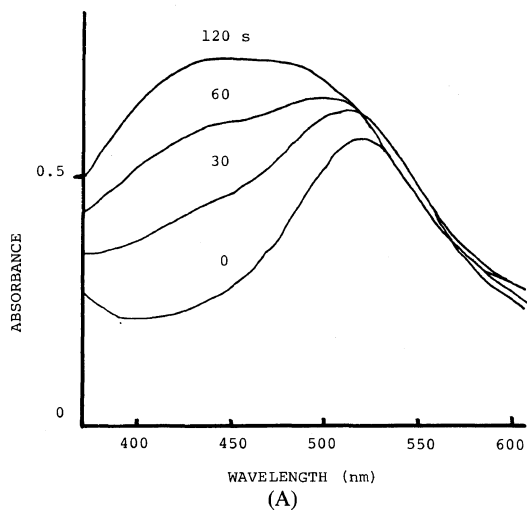
showed a pronounced suppression effect as DMF did. One interesting feature here is that the presence of a small amount of VB^{2+} exhibits strong inhibition on the polymerization. Since the plasma-exposed VPdn can reduce BV^{2+} in the same manner as DMF, the results suggest that the active species is directly associated with a product capable of reducing BV^{2+}. Thus, the solvated ion radicals or electrons may be considered at least as transient intermediates for the successive radical polymerization. Direct observation of these species in DMF or VPdn is left pending for further investigation.

It should, also be mentioned that a significant increase in the electric conductivity is observed when DMF is exposed to plasma as shown in Figure 3. As shown in this figure, the conductivity increased to more than 17 times that of the initial DMF by the plasma exposure as short as 300 s. This result may be considered in relation to the presence of ions since no evidence of a reaction product due to plasma exposure has been detected in DMF by gas chromatography.

Radicals (or electrons) present in DMF by

plasma were found to be efficiently trapped by DPPH. The progressive spectral changes in DPPH with plasma duration are shown in Figure 4A. The similar spectral changes were obtained when DMF was initially exposed to the plasma, followed by subsequent mixing with DPPH. Rather rapid spectral changes were observed in this case (Figure 4B). A spectral change was also observed when AIBN was thermally decomposed to form 2-cyano-2-propyl radicals in the presence of DPPH (Figure 4C). However, the rate of the spectral changes due to AIBN was much slower compared with those obtained by the plasma. It was calculated that the rate of consumption of DPPH was 1×10^{-5} mol l^{-1} s per 1 cm^2 surface for the plasma at 100 W and 4.4×10^{-8} mol l^{-1} s for 10^{-3} mol l^{-1} of AIBN at 50°C. Since the rate of consumption of radicals formed by the plasma is proportional to the scavenger's concentration as reported previously,[13] one can roughly estimate that the concentration of the radicals liberated in the plasma at 100 W and diffused successively through 1.0 cm^2 of the liquid surface is about 2300 times higher than that formed by the decomposition of 10^{-3} mol l^{-1} AIBN at 50°C in DMF. This result indicates that enormous number of radicals are generated in a short duration of plasma and then diffusing readily through the surface, they induce subsequent reactions with DPPH or postpolymerization. It should also be noted that the plasma-initiated polymerization in water is effectively depressed by the presence of HQ as shown in Figure 5.

A mechanism can now be envisioned in terms of eq 1—7 in Table II from the results of the polymerization.

M_G* represents the species formed as a result of the direct interaction of the monomer vapor with energetic electrons in the gas phase. Some of them can then diffuse to the liquid phase and become M_L*. The reaction of electrons with the solvent may probably be neglected in the process of the polymerization since polymerization by the plasma takes place very selectively with the monomers susceptible to radical polymerization. Moreover, it was previously reported[3] that plasmas generated from inorganic gases such as N_2, Ar and He cannot induce polymerization, but only the plasma generated from the monomer vapor is capable of initiating the polymerization of the monomer.
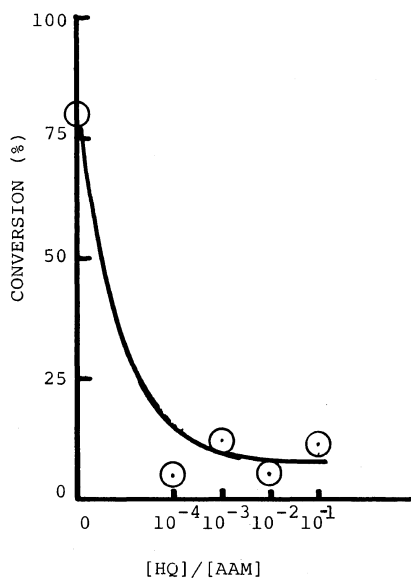

Figure 5. Plasma-initiated polymerization of acrylamide (AAM) in water in the presence of hydroquinone (HQ): Plasma, 100 W, 60 s; postpolymerization, 25°C, 4 h; AAM, 4.15 mol l^{-1}.

Table II. Proposed mechanism of plasma-initiated solution polymerization

Gas phase	$M_G + e \rightarrow M_G^*\ (+e)$	(1)
Gas-liquid interphase	$M_G^* \xrightarrow{\text{Diffusion}} M_L^*$	(2)
Solvation of reactive species	$M_L^* + S \rightarrow (M_L^*)_S$	(3)
Initiation	$(M_L^*)_S + M_1 \rightarrow (M_1^*)_S$	(4)
or	$(M_L^*)_S + M_1 \rightarrow M_1^*$	(5)
Propagation	$(M_1^*)_S + M_2 \rightarrow (M_2^*)_S$	(6)
or	$M_1^* + M_2 \rightarrow M_2^*$	(7)

Activity of $(M_L^*)_S$	Very high	Low	Very low
	$(M_L^*)_{H_2O}$	$(M_L^*)_{ethanol}$ $(M_L^*)_{DMSO}$	$(M_L^*)_{DMF}$ $(M_L^*)_{VPdn}$

M_G^*, M_L^*, Monomer and its derivatives in gas and liquid phase, respectively. $(M_L^*)_S$, solvated active specie; M_1, M_2, monomer; S, solvent.
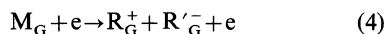
It may be possible that M_G* is any ion formed by electron attachment, since this process occurs at the lowest electron energy by electron resonance capture.[14]
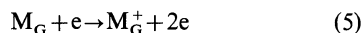
$$M_G^\cdot + e \rightarrow M_G^-$$ (2)

This ion may dissociate to give a neutral radical and a negative ion.

$$M_G^- \rightarrow R_G^\cdot + R'^-_G \qquad (3)$$
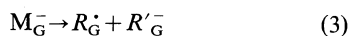
At higher energies, the production of cations may also occur.

$$M_G + e \rightarrow R_G^+ + R'^-_G + e \qquad (4)$$

or

$$M_G + e \rightarrow M_G^+ + 2e \qquad (5)$$

$$M_G^+ \rightarrow R_G^+ + R'^\cdot_G \qquad (6)$$

where R_G and R'_G may be any monomer derivatives or hydrogen atom.

It should be considered that the activity of $(M_L^*)_S$ and consequently, its lifetime is strongly influenced by the solvent. Thus, polymerization should be closely associated with the activity of the solvated species, which then form the growing radicals M_p^* as a result of subsequent reactions with the monomer. It is supposed from the experimental results that the activity of $(M_L^*)_S$ must be very high in water, but extremely low in DMF. It is not clear at present whether or not the active species are responsible for the chain propagation. M_p^* also is affected by the solvent as commonly observed in ionic polymerizations (eq 6 in Table II) or propagates in a free mechanism without strong solvation (eq 7 in Table II).

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