

Plasma-Induced Copolymerization of Hydrochloride of *N,N*-Dimethylaminoethyl Methacrylate and Acrylamide

JIANMEI LU, ZHENPING CHENG, XIULIN ZHU, LIFEN ZHANG

Department of Chemistry, Suzhou University, Suzhou, 215006, People's Republic of China

Received 14 December 2000; accepted 1 April 2001

ABSTRACT: A super alcohol-absorbing resin, with absorbency of 106 g/g for methanol, was polymerized from the hydrochloride of *N,N*-dimethylaminoethyl methacrylate (DM) and acrylamide (AM) by plasma-induced polymerization at lower temperatures in water solutions. Many factors affecting the absorbing properties, such as post-polymerization time, monomer concentration, plasma duration, plasma discharge power, monomer ratio, et al., were studied. The reasons for the absorbing alcohol of resins was also discussed. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 84: 729–734, 2002; DOI 10.1002/app.10086

Key words: plasma initiated copolymerization at lower temperatures; super alcohol-absorbing resin; hydrochloride of *N,N*-dimethylaminoethyl methacrylate; acrylamide; property

INTRODUCTION

Osada et al.¹ investigated plasma-induced polymerization first. In a typical case, the vapor phase of a monomer liquid in a sealed tube is used to create a plasma. The duration of a plasma is generally very short (on the order of a few seconds). After plasma exposure, the tube is shaken to mix plasma-induced reactive species, which act as initiators of polymerization, with the monomer. The tube is kept at a constant temperature for a prolonged period of time. Results indicate that plasma-induced polymerization is a free-radical addition polymerization initiated by difunctional free radicals created by plasma. In recent years, the studies of plasma-induced polymerization mainly concentrated on the mechanisms² of polymerization and the selectivity for monomers, and less on liquid-absorbing resins.³ The super alcohol-absorbing resin, which is a new concept — it can absorb not only water but also a wide variety of alcohol — has not been reported.

In this paper, hydrochloride of *N,N*-dimethylaminoethyl methacrylate (DM) and acrylamide (AM) were selected as monomers of copolymerization by plasma-induced polymerization in water solutions, and the copolymer obtained can be used as super alcohol-absorbing resins. The effects of post-polymerization time, monomer concentration, plasma duration, plasma discharge power, and monomer ratio on the absorbencies for alcohol have been investigated.

Because the obtained resins don't contain substances such as initiators, organic solvents, etc., they have very high purity, which provides a new method for synthesizing functional polymers for special use.

EXPERIMENTAL

Materials

AM and *N,N'*-methylene bisacrylamide were recrystallized and DM was purified by removal of inhibitor by a standard procedure followed by vacuum distillation. Hydrochloric acid, glycol, methanol, chlorohydrin, ethanol, *n*-propyl alcohol, *n*-

Correspondence to: J. Lu (Lujm@suda.edu.cn).

Journal of Applied Polymer Science, Vol. 84, 729–734 (2002)
© 2002 John Wiley & Sons, Inc.

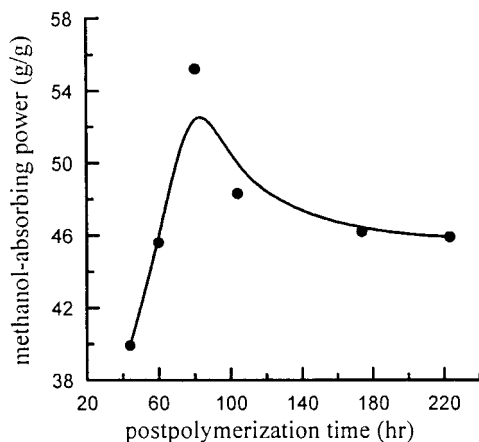


Figure 1 Relationship between post-polymerization time and methanol-absorbing power of resin 1. Polymerization conditions: plasma, 100 W; 50 s; $m(\text{AM}):m(\text{DM}) = 1:4$; monomer concentration = 38 wt %; post-polymerization, 25 °C.

butyl alcohol, benzyl alcohol, benzene, dimethylsulfoxide, cyclohexane, etc. were purchased from commercial sources and are analytical reagents.

Preparation of Reactive Liquid

Hydrochloric acid was slowly added in aqueous solutions of DM until the pH of the solutions was 3.0, then the hydrochloride of DM was obtained. AM or *N,N'*-methylene bisacrylamide was added in the hydrochloride of DM, respectively, and mixed uniformly, then the reactive liquids A or B were prepared, respectively.

Plasma-Induced Polymerization

The experimental apparatus and procedure used in the present investigation were essentially with those reported by Osada et al.¹ The reactive liquids A or B prepared were poured into a thin-walled ampoule, deaerated by repeated freezing and thawing while under a vacuum of 10^{-4} – 10^{-5} Torr, and finally sealed in liquid nitrogen. The sealed ampoule was inserted between a pair of parallel plate electrodes connected to a radio-frequency capacitive-coupled glow discharge system, which operated at 43.54 MHz and delivered up to 200 W. As soon as the system was regulated to the assigned power, a glow discharge was initiated in the space in the ampoule. After the plasma initiation or exposure, which was generally conducted at room temperature, the ampoule was taken out and thawed, then shaken to mix plasma-induced reactive species with the reactive liquids and kept at 25 °C for post-polymerization. After post-poly-

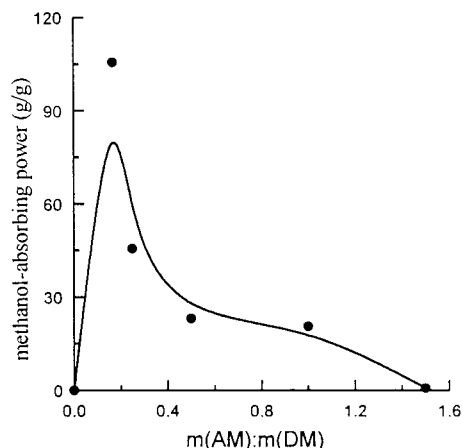


Figure 2 Relationship between monomer ratio and methanol-absorbing power of resin 1. Polymerization conditions: plasma, 100W, 50 s; monomer concentration = 38 wt %; post-polymerization, 61 h, 25 °C.

merizing for a definite time period, the ampoule was opened and the polymer (gel) was precipitated with acetone and filtered, and then dried in a vacuum oven at 50 °C. The alcohol-absorbing resin 1 or 2 (resin 1, copolymer obtained by reactive liquids A; resin 2, homopolymer obtained by reactive liquids B) was obtained. The absorbencies of resins were determined by the following method: 0.1 g of resins was added in 100-mL alcohol solutions at 25 °C for 1 h, and then the swelled gel was filtered and weighed, and the absorbencies of resins were calculated according to

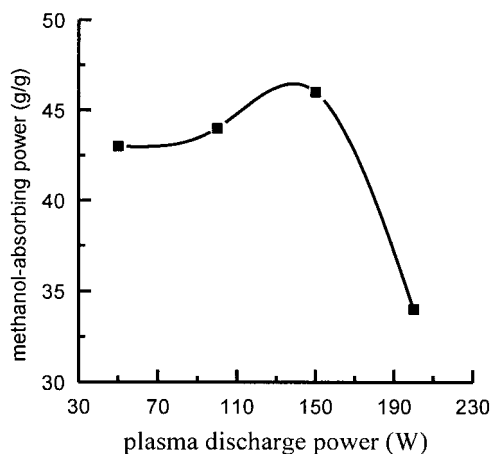


Figure 3 Relationship between plasma discharge power and methanol-absorbing power of resin 1. Polymerization conditions: plasma, 30 s; $m(\text{AM}):m(\text{DM}) = 1:4$; monomer concentration = 38 wt %; post-polymerization, 60 h, 25 °C.

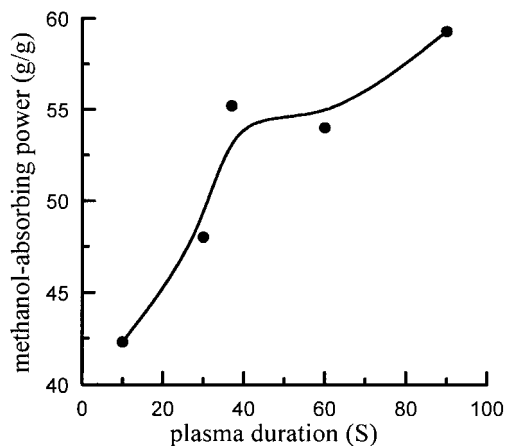


Figure 4 Relationship between plasma duration and methanol-absorbing power of resin 1. Polymerization conditions: plasma, 100 W; m(AM):m(DM) = 1:4; monomer concentration = 38 wt %; post-polymerization, 80 h, 25 °C.

$$G = (W - 0.1)/0.1 \text{ (g/g)} \quad (1)$$

where G is the alcohol-absorbing power of the resin, and W is the weight of the swelled gel.

RESULTS AND DISCUSSION

Comparison with Normal Radical Polymerization

Generally speaking, the main features of plasma-induced polymerization were considered as active radical polymerization, whereas the normal radical polymerization using the initiators such as AIBN was not. Experimental results in our study indicated that the polymerization rate of the selected system discussed here was lower than that of the normal radical polymerization. The former, reaching the conversion of almost 100%, polymerized ~40 h, whereas the latter polymerized for only ~3 h.

Effect of Post-Polymerization Time

Figure 1 is a plot of methanol-absorbing power as a function of time for the plasma-induced polymerization, using a 100W, 50S plasma exposure and 25 °C post-polymerization temperature. At this temperature, the rate of thermal polymerization is exceedingly small, so there should be little "interference" from the thermal reaction in these experiments. The most interesting feature of this plot is that the absorbing power has a maximum at a little under 56 g/g for post-polymerization

times well in excess of 80 h. The plasma-induced reaction continues to total conversion (the conversion of all polymers synthesized in this study are ~100%) and eventually yields cross-linked polymers. A super alcohol-absorbing resin is a cross-linked polymer with three-dimensional networks, and its absorbencies not only depend on the chemical structures of the polymer but also on the capacity of a network; namely, the degree of cross-linking of the polymer.⁴ The degree of cross-linking should have an optimum. On the one hand, if the degree is too small, the length of a linear chain of polymers between the closest two cross-linked points is consequently very long, which means an increase in the solubility of the polymer so that the absorbing power decreases accordingly. On the other hand, if the degree is too large, the capacity of a network will be too small and, accordingly, that the power decreases as well. It is very obvious that the degree increases with the prolonging of post-polymerization time. As a result, a maximum in power is reached at the point when the degree is appropriate. Both increasing and decreasing the post-polymerization time result in sharp drops of the absorbencies.

Effect of Monomer Ratio

Figure 2 is a plot of methanol-absorbing power as a function of the weight ratio of AM to DM in reactive liquids A. It can be seen from this graph that a maximum in methanol-absorbing power (~100 g/g) is reached at the point when the ratio

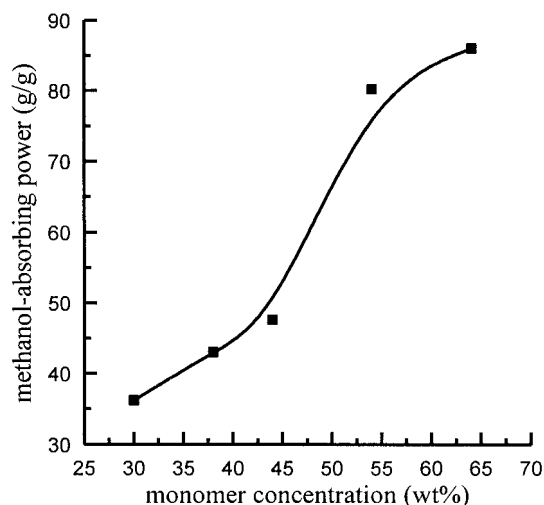


Figure 5 Relationship between monomer concentration and methanol-absorbing power of resin 1. Polymerization conditions: plasma, 100 W, 45 s; m(AM):m(DM) = 1:4; monomer concentration = 38 wt %; post-polymerization, 63 h, 25 °C.

Table I Absorbencies for Different Alcohols

Parameter	Deionizing Water	Glycol	Methanol	Chlorohydrin	Ethanol	<i>n</i> -Propyl Alcohol	<i>n</i> -Butyl Alcohol	Benzyl Alcohol
Dielectric Constant (20°C)	80.1	37.7 (25°C)	33.62	26.0	25.0	20.1 (25°C)	17.8	13.1
Absorbency (g/g)	420	137	86	20	0	0	0	0

m(AM):m(DM) is 1:6. The most outstanding feature of this graph is that the absorbing power is 0 (because the polymer is linear and soluble) when the ratio is 0 (in fact, the polymer is a homopolymer of hydrochloride of DM, but it is very different from the resin 2 already mentioned above because *N,N*-methylene bisacrylamide was not added in this system) as well. This result indicates that AM also acts as the cross-linking agent of polymerization in this system of plasma-induced copolymerization. The reason is that the α -H in the structure of AM is very active and it can easily depart from the structure. Therefore, the capacities of cross-linked networks of resins should also have an optimum value with the increase of the amount of AM. As a result, the absorbing power should have an optimum value accordingly. In addition, when the ratio continues to increase to 1.5:1, the resin obtained is a copolymer with the degree of highly cross-linking so that its corresponding absorbency is nearly 0.

Effects of Plasma Discharge Power and Plasma Duration

Data concerning the effects of the conditions of the glow discharge on the plasma-induced polymerization reaction are shown in Figures 3 and 4. The scope of this study didn't permit a thorough examination of all variables pertinent to glow discharge chemistry. However, two of the most important variables were studied, the discharge power and the plasma duration.

Figure 3 shows the effect of plasma power on methanol-absorbing power of the resins when a plasma exposure time of 30 s and a post-polymerization time of 60 h are used. The absorbency goes through a maximum when plotted against plasma power. The increase in absorbency with increasing plasma power observed at low powers can be attributed to the formation of an increasing amount of initiators (reactive species).⁵ A maximum in absorbency is reached at the point when the power is great enough to degrade initiators produced during the initial period of exposure of monomers to the plasma. This result is because the polymerization rate changes much more sharply with the amount of initiators and the degree of cross-linking reaction changes with the rate accordingly in the same post-polymerization time. The result is that a cross-linked network of polymers with an appropriate capacity should be formed.

Figure 4 illustrates a plot of methanol-absorbing power as a function of plasma duration (or glow discharge exposure time) for experiments utilizing a discharge power of 100 W and a polymerization time of 80 h. A nearly linear increase in absorbency with increased plasma duration is seen. The explanation is fairly straightforward. Increasing plasma duration means the formation of a much higher amount of initiators⁵ that results in the increase of degree cross-linking reaction and the methanol-absorbing power.

Table II Absorbencies for Ethanol-Water Solutions with Different Concentration

Parameter	Weight Percent					
	10	30	50	71.9	88.5	100
Dielectric Constant (25°C)	72.8	61.1	49.0	37.0	27.4	24.3
Absorbency (g/g)	400	260	151	100	31	0

Table III Absorbencies for Some Solvents

Parameter	Dimethylsulfoxide	Benzene	Cyclohexane	Kerosene	Gasoline
Absorbency (g/g)	73	0	0	0	0

Effect of Monomer Concentration

Figure 5 shows a plot of methanol-absorbing power as a function of monomer concentration, at constant plasma conditions of 100 W discharge power and 45 s exposure time and a constant post-polymerization time of 63 h. It can be seen from the graph that the absorbing power increases with the concentration. The plausible explanation for this result involves two aspects. On the one hand, the viscosity of plasma-induced reaction mixtures increases with the concentration that the ability of cross-linking reaction increases. On the other hand, increasing the concentration would be in favor of encounters among growing chains or molecules of monomers that the rate of polymerization accelerates sharply. The two factors would result in the increase of the degree of cross-linking reaction. This result also implies that the absorbing power increases.

Absorbencies for Various Alcohol

Tables I, II, and III present the effects of various solvents on the absorbing power of the same sample of resin 1. The sample was produced via plasma exposure at 100 W for 50 s, monomer ratio m(AM):m(DM) at 1:4, and the monomer concentration at 64 wt %, followed by post-polymerization at 25 °C for 63 h.

Table I shows the absorbencies for several kinds of alcohol. It is theorized that the mechanism of super alcohol-absorbing resins is similar to that of the super water-absorbing resins. Super alcohol-absorbing resin is a three-dimensional network polymer with hydrophilic groups and

polyelectrolytes as well. When an alcohol liquid meets with it, the network will expand because of the hydration between the alcohol liquid molecules and the hydrophilic groups of polymers. Consequently, an osmotic pressure between inside and outside in the gel will be produced because of the difference of the concentration of ions, and the alcohol molecules will penetrate into the networks and be absorbed. It can be seen from the table that the absorbencies are pertinent to the dielectric constants of corresponding solvents, and the absorbency increases with the dielectric constant. This result is because the polarity of the alcohol is relevant to the dielectric constants. The alcohol with larger dielectric constants, such as glycol, methanol, etc., has a stronger hydration with the hydrophilic groups of polymers so that the corresponding absorbing powers are larger. The most interesting feature of this table is that the resin in this study can't absorb the alcohol liquids with smaller dielectric constants, such as ethanol, *n*-propyl-alcohol, *n*-butyl-alcohol, benzyl alcohol, etc. This result indicates that the hydration between the hydrophilic groups of polymers and those liquids is so weak that the networks can not be unclosed effectively and those liquids can not be absorbed. The available evidence also suggests that the other alcohol liquids, with smaller dielectric constants than those just mentioned, shouldn't be absorbed.

However, the ethanol solutions presented in Table II can be absorbed well. It is obvious that water increases the polarity of ethanol solutions so that the absorbing powers increase as well. It is also seen from the Table II that the absorbencies

Table IV Relationships between Various Resins Polymerized by Plasma-Induced Polymerization and Properties of Absorbing Water or Alcohol^a

Monomer	DM ⁺ -CO-AM	DM	DM ⁺	DM-CO-AM	AM	AA	DM ⁺ -CO-AA
Properties of							
Absorbing Liquid							
Water	✓	✓	✓	✓	✓	✓	✓
Methanol	✓	×	✓	×	×	×	✓

^a DM, *N,N*-dimethylaminoethyl methacrylate; AM, acrylamide; AA, acrylic acid; DM⁺, hydrochloride of *N,N*-dimethylaminoethyl methacrylate; only homopolymer of DM⁺ (resin 2 mentioned above) contained the cross-linking agent (*N,N'*-methylene bis-acrylamide), and any other polymer didn't. Key: (✓) absorbs well; (×) cannot absorb.

increase with the dielectric constants of ethanol solutions. The results, alternatively, demonstrate the viewpoint already mentioned.

In Table III it is shown that a non-alcohol solvent (dimethylsulfoxide, dielectric constant: 46.7 at 25 °C) can also be absorbed well, with an absorbency of 73 g/g, but that the other solvents, such as benzene, cyclohexane, kerosene, gasoline, etc., cannot be absorbed. The reason for this result is that oxygen atoms in dimethylsulfoxide molecules have a stronger ability of hydration with the hydrophilic groups of polymers than those in the latter solvents.

Reason for Absorbing Alcohol

In this final section, we offer some informed speculations regarding the reasons for absorbing alcohol. Generally speaking, the average super water-absorbing resins don't have the ability to absorb alcohol, but the super alcohol-absorbing resins obtained in this study can absorb not only water but also alcohol. Table IV presents the properties of absorbing water or alcohol of various resins obtained by plasma-induced polymerization. It can be seen from the results in Table IV that all resins can absorb water, but only those resins with positive ion groups ($N^+(CH_3)_2$) in their structures can absorb alcohol. It is fully believed that it is the positive ion groups ($N^+(CH_3)_2$) in resins that

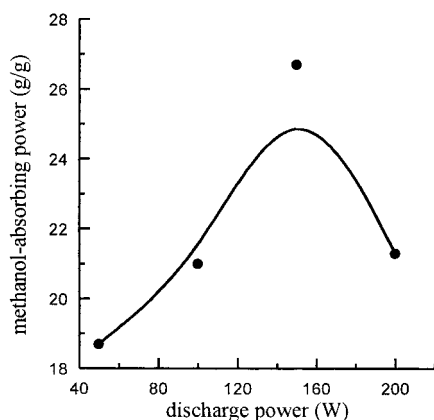


Figure 6 Relationship between discharge power and methanol-absorbing power of resin 2. Polymerization conditions: plasma, 60 s; monomer concentration = 40 wt %; amount of cross-linking agent, 0.1 wt %; post-polymerization, 28 h, 25 °C.

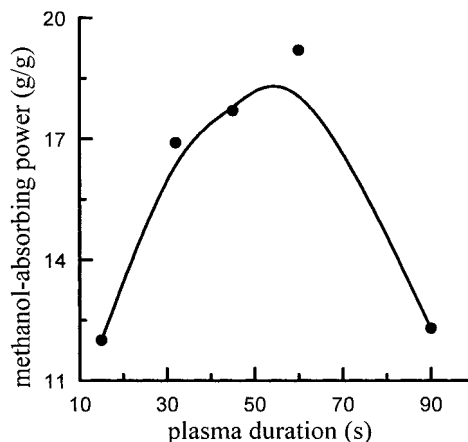


Figure 7 Relationship between plasma duration and methanol-absorbing power of resin 2. Polymerization conditions: plasma, 50 W; monomer concentration = 40 wt %; amount of cross-linking agent, 0.1 wt %; post-polymerization, 28 h, 25 °C.

result in the super alcohol-absorbing property of the resins.

In addition, we want to point out that the homopolymer of DM^+ (resin 2), using *N, N*'-methylene bisacrylamide as cross-linking agent and polymerizing by plasma-induced polymerization, can also be used as super alcohol-absorbing resins. The effects of two of the most important variables pertinent to glow discharge chemistry, the discharge power and the plasma duration, on the absorbencies of resin 2 are shown in Figures 6 and 7, respectively. The tendencies of two graphs are basically similar to the Figures 3 and 4. However, a maximum in absorbency is reached in Figure 7. This result indicates that the plasma duration in this reaction has an optimum, and both decreasing and increasing plasma duration will result in sharp drops of the absorbencies.

REFERENCES

- Osada, Y.; Bell, A.T.; Shen, M. *J Polym Sci, Polym Lett Ed* 1978, 16, 309.
- Osada, Y.; Takase, M.; Iriyama, Y. *Polym J* 1983, 1, 81.
- Kohjin Company, Ltd., *Jpn. Kokai Tokyo Koho*, Jp: 59193911, 1984.
- Flory, P.J. *Principles of polymer chemistry*; Cornell University Press: New York, 1953.
- Paul, C. W.; Bell, A. T.; Soong, D. S. *Macromolecules* 1985, 18, 2312; 1986, 19, 1431.