

Low Temperature Plasma-Initiated Precipitation Copolymerization of Styrene and Maleic Anhydride

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ABSTRACT: In this study, we show that the plasma-initiated polymerization (PIP) can be carried out at ambient pressure using the dielectric barrier discharge (DBD) technology. The structure of styrene-maleic anhydride copolymer (SMA) is analyzed by ^1H and ^{13}C -NMR. The effects of initiation time, gas flow rate, post-polymerization time, and temperature on yield are also discussed. The results show that SMA exhibits a dominant alternating structure. The yield of SMA increases with the increase of initiation time and polymerization temperature, remains unchanged

with the increase of flow rate, and decreases rapidly with the increase of St-MAH molar ratio. The PIP in this experiment is shown to follow the free-radical polymerization mechanism and the process of the polymerization is also discussed. © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 125: 1352–1356, 2012

Key words: plasma-initiated polymerization; styrene-maleic anhydride copolymerization; dielectric barrier discharge

INTRODUCTION

In the last thirty years, plasma-initiated homopolymerization and copolymerization (PIP) have attracted much research interest.^{1–10} This method has unusual kinetic behavior, e.g., the polymerization can last for extended periods (even months)⁸ and can produce ultra high molecular weight polymers,^{1–3,9} such as poly(methylmethacrylate) with the molecular weights as high as 10^7 g/mol. Although the mechanism involved in PIP is unknown,⁷ it is widely accepted that the PIP proceeds via a free-radical mechanism.^{1–10}

Although many researchers have focused on PIP, little progress has been made in this area.¹⁰ In traditional PIP, plasma polymerization must be initiated by igniting low-pressure plasma in the vapor space above the frozen monomer under high vacuum, followed by propagation at room temperature. This method is not cost effective and it is too complicated to be followed by industry.

In our present study, we are trying to investigate PIP under ambient pressure by using the dielectric barrier discharge (DBD) technology. This method may provide a convenient PIP technique. It is possi-

ble to control the initiation process, i.e., we can re-initiate residual monomer polymerization to increase the conversion yield and/or produce functional polymers by re-initiating and re-pouring them into different monomers, and it is applicable to the polymerization of some monomers that are difficult to polymerize with conventional plasma method. With these considerations, it is possible for PIP to be realized on an industrial scale. In this article, the copolymerization of styrene (St) and maleic anhydride (MAH) was continually initiated by plasma at ambient temperature and pressure, and alternative copolymers were obtained.

EXPERIMENTAL

Materials and equipment

St was washed thrice with a 10% NaOH aqueous solution to remove inhibitor, stored in fridge-freezer after drying over calcium chloride, and then was freshly distilled under reduced pressure just before use. MAH was recrystallized twice from chloroform. All of the monomers and solvents were bought from Kerisi Company (Tianjin, China). Free radical catching agent, 2,2-diphenyl-1-picrylhydrazyl (DPPH, Sigma-Aldrich Co., St. Louis, MO), was used as received.

Styrene and MAH copolymerization

Prior to the experiment, the mixture of St, MAH, and xylene were successively added into a reactor and stirred until MAH was dissolved in the solution

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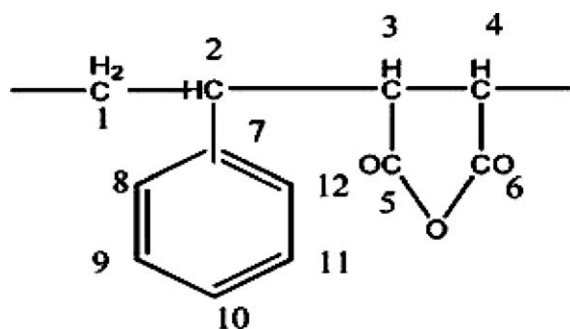


Figure 1 Structure of St-MAH copolymer.

(St = 15 mL, xylene = 50 mL). CO₂ (99.995%) controlled by the mass flow controller was pumped into the reactor to remove air inside. The plasma set-up yielded glow discharges from the radio frequency generator (self-made, 13.56 MHz) with the cooperation of the outer electrode surrounding the quartz tube and the inner electrode which was brass wires. Unlike others, the experimental process was conducted at atmospheric pressure. When switched on the plasma generator, remote plasma was injected into the solution in the three-necked round bottom flasks to initiate the polymerization of St and MAH at the set temperature.

After the postpolymerization was carried out for a prescribed time, styrene-maleic anhydride (SMA) precipitation was washed by xylene three times and then washed with ethanol for another three cycles to remove the excess monomers. SMA products were dried at 313 K in a vacuum over 24 h. The structure of SMA was shown in Figure 1.

In this study, the weight of SMA was measured gravimetrically, and the reaction yield was calculated as follows:

$$\text{Yield (\%)} = W_p / (W_s + W_m) \times 100\% \quad (1)$$

where W_p , W_s , and W_m are the weights of SMA, St, and MAH, respectively.

Free-radical catching agent, DPPH, was added into the solution at the concentration of 5 mg/mL before the plasma initiation to determine whether the agent could quench the polymerization during the PIP process.

NMR measurements

The composition of SMA was determined by ¹H and ¹³C-NMR spectra on a Varian Inovia 500 MHz NMR spectrometer using acetone-*d*₆ as solvent, and tetramethylsilane was used as an internal standard. Distortionless enhancement by polarization transfer (DEPT) spectra were obtained using the following combination of the $\pi/4$ and $3\pi/4$ experiments: CH₂ = $(\pi/4) + 1.15 (3\pi/4)$.

Intrinsic viscosity of dilute solution

Because copolymer could not dissolve in tetrahydrofuran and water, the intrinsic viscosity of dilute solution was used to determine the viscosity average molecular weight, M_{η} , which was calculated using the Mark-Houwink equation for SMA in acetone at 303 K¹¹:

$$[\eta] = K\overline{M}_{\eta}^{\alpha} \quad (2)$$

where $K = 8.69 \times 10^{-5}$ dL/g (= 100 mL/g), $\alpha = 0.74$.

RESULTS

¹H-NMR analysis

Figure 2 shows the ¹H-NMR spectrum of SMA. In the spectrum, $\delta = 3.0$ – 3.8 and 6.0 – 7.7 corresponded to the two methine protons in MAH unit and the aromatic protons of the St, respectively, which were the evidence for the formation of SMA. Generally, the chemical shift of methylene peaks of polystyrene backbone with SSM, MSS, and SSS sequences appeared at 1.16–1.63 ppm and that of methine and methylene protons of St unit in the SMS sequence appeared at 1.6–3.0 ppm (S = St unit, M = MAH unit). In Figure 2, a broad peak signal appeared at 1.6–3.0 ppm while small peaks appeared at 1.16–1.63 ppm. The above results indicated that the structure of our sample's main chain was SMS, but the structure of SSM, MSS, SSS in the copolymer could not be excluded because of the chemical shift signals at 1.16–1.63 ppm.¹² The formation of the alternating structure of the SMA compositions of the copolymer

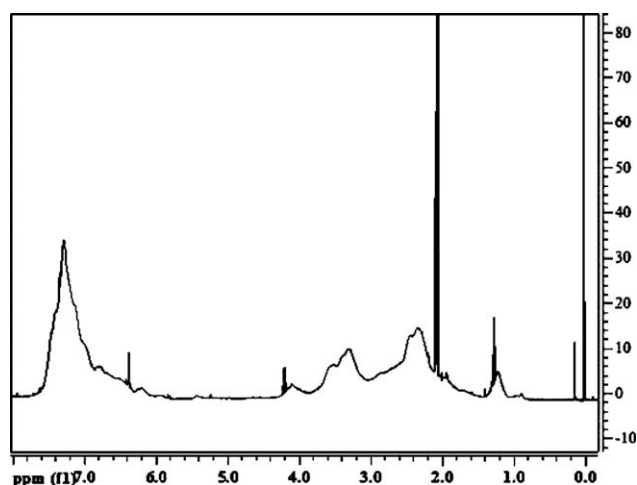


Figure 2 ¹H-NMR spectrum of St-MAH copolymer. (Monomer molar ratio of St and MAH: 1 : 1; discharge power: 20 W; initiation time: 30 min; CO₂ flow rate: 80 mL/min; postpolymerization time: 1 h; polymerization temperature: 303 K).

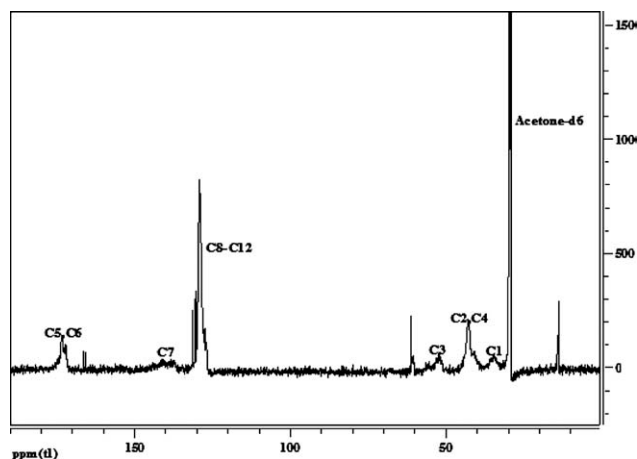


Figure 3 ^{13}C -NMR spectrum of St-MAH copolymer. (Monomer molar ratio of St and MAH: 1 : 1; discharge power: 20 W; initiation time: 30 min; CO_2 flow rate: 80 mL/min; postpolymerization time: 1 h; polymerization temperature: 303 K).

prepared from the PIP was calculated according to the following equation¹²:

$$\text{MAH \%} = 5 \times I_{3.4} / (2 \times I_{7.0} + 5 \times I_{3.4}) \quad (3)$$

where $I_{3.4}$ and $I_{7.0}$ were integral values of the peaks that appeared at 3.0–3.8 and 6.0–7.7 ppm, respectively. MAH% was the molar percentage of MAH in the copolymer. The result, which was about 46.5% of the content of MAH in this copolymer, confirmed the conclusion above.

^{13}C -NMR analysis

Figure 3 showed a typical ^{13}C -NMR spectrum of a SMA where the peaks were assigned with the chemical shifts according to Qiu et al.¹³ Indeed, the quaternary carbon of St exhibited a main peak between 136 and 140 ppm related to the alternating M-S-M sequence; no peak corresponding to M-S-S or S-S-S sequence appeared between 142 and 145 ppm. In the aliphatic carbons region, the ^{13}C -NMR spectrum did not give sufficient sequence information because the signals of methine and methylene carbons were partially overlapped. However, sequence information could be obtained from DEPT experiments by recording the spectra at $\pi/4$ and $3\pi/4$, and then combining them together: $\text{CH}_2 = \pi/4 + 1.15(3\pi/4)$. For SMA, three distinct CH_2 regions, 33–37, 37–42, and 42–47 ppm, were assigned to M-S-M, S-S-M + M-S-S, and S-S-S sequences, respectively.^{14,15} Figure 4 showed the methylene spectrum of the SMA. One broad methylene signal at 33–37 ppm of M-S-M was observed, demonstrating that the St-MAH copolymers possessed the alternating sequence structure.

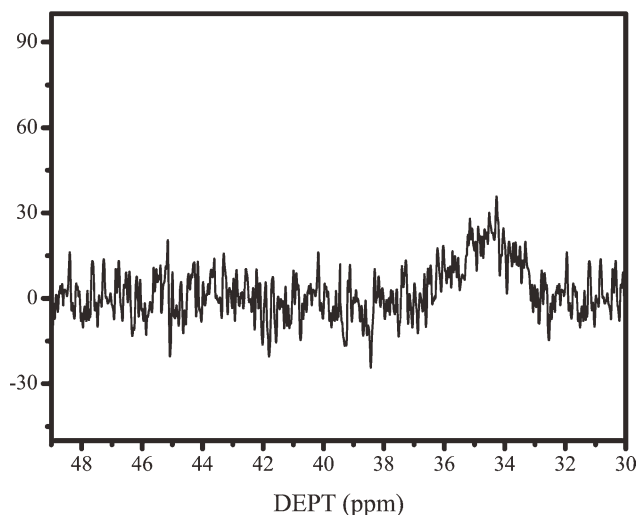


Figure 4 DEPT spectrum of St-MAH copolymer. (Monomer molar ratio of St and MAH: 1 : 1; discharge power: 20 W; initiation time: 30 min; CO_2 flow rate: 80 mL/min; postpolymerization time: 1 h; polymerization temperature: 303 K).

Effects of initiation time, flow rate, and polymerization temperature

The yield increased with the extension of initiation time and the increase of polymerization temperature and remained unchanged with the increase of flow rate. However, prolonging initiation time and increasing the flow rate had limited effects on the molecular weight of the copolymer (Figs. 5 and 6). This could be explained by the free radical polymerization mechanism of fast propagation and rapid termination. The molecular chain might be formed immediately after the initiation.

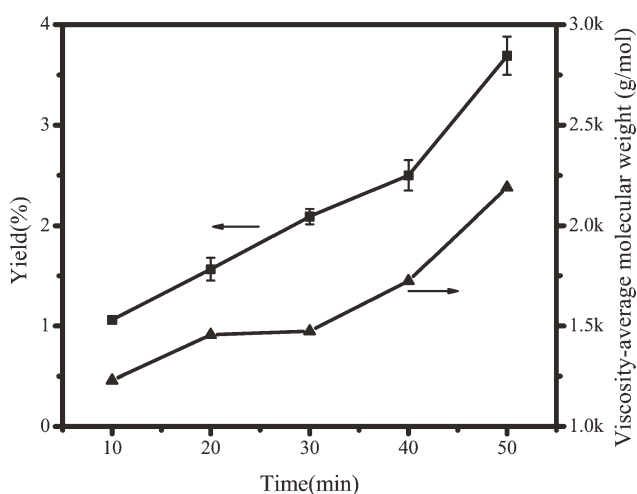


Figure 5 Effects of initiation time on yield and viscosity average molecular weight. (Monomer molar ratio of St and MAH: 1 : 1; discharge power: 20 W; CO_2 flow rate: 80 mL/min; postpolymerization time: 1 h; polymerization temperature: 303 K).

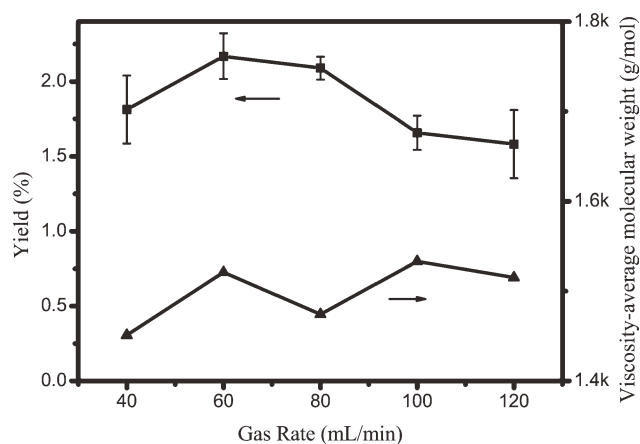


Figure 6 Effects of flow rate on yield and viscosity average molecular weight. (Monomer molar ratio of St and MAH: 1 : 1; discharge power: 20 W; initiation time: 30 min; postpolymerization time: 1 h; polymerization temperature: 303 K).

From the result of Figure 7, the molecular weight of the copolymer decreased with increasing temperature to 323 K. That might be due to increasing chain transfer rate constant with the increase of temperature.

Effects of the postpolymerization time

The postpolymerization was carried out to study whether prolonging reaction time could increase the molecular weight since it had been reported that the active species could last for even several months.⁸

Figure 8 displayed the effect of postpolymerization time on yield and viscosity average molecular weight. At this temperature, the rate of thermal polymerization was extremely low. Thus, there should

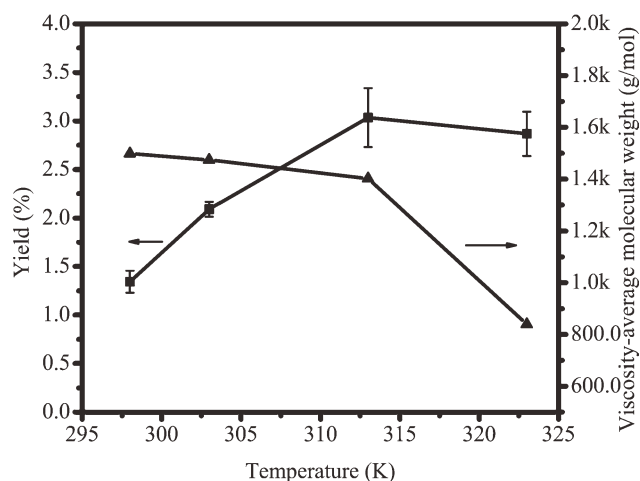


Figure 7 Effects of polymerization temperature on yield and viscosity average molecular weight. (Monomer molar ratio of St and MAH: 1 : 1; discharge power: 20 W; initiation time: 30 min; CO₂ flow rate: 80 mL/min; postpolymerization time: 1 h).

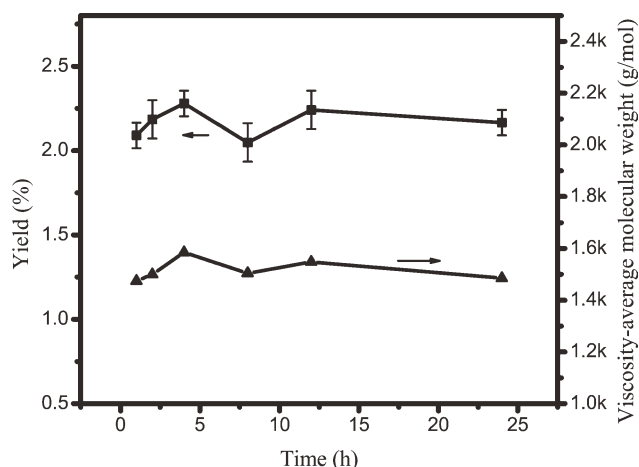


Figure 8 Effects of postpolymerization time on yield and viscosity average molecular weight. (Monomer molar ratio of St and MAH: 1 : 1; discharge power: 20 W; initiation time: 30 min; CO₂ flow rate: 80 mL/min; polymerization temperature: 303 K).

be little effect from the thermal reaction in these experiments. The result from Figure 8 indicated that there was no obvious variation of yield and molecular weight with postpolymerization time, even postpolymerization time in excess of 24 h. This feature was different from that of PIP. As we know from PIP, the yield and molecular weight increased with the increase of postpolymerization time and then ultrahigh molecular weight polymer could be formed due to the long life of the initiator produced by plasma, which could last for even several months.^{1-3,8,9} However, Paul³ concluded that the long duration of PIP was not due to the continuous generation of initiating radicals but rather to a reduction in the chain termination rate constant, chain ends were formed more frequently by chain transfer to monomer during this period. The results of electro spin resonance spectroscopy reported by Yang et al.⁹ proved this observation and You et al.¹⁶ found that the chain transfer reaction was the dominate factor in PIP reaction. According to the above conclusions, the unchanged yield and molecular weight would be due to the precipitation of SMA, which blocked the radical transfer from chain to monomer.

Effects of the molar ratio

The conversion decreased rapidly with the increasing of St-MAH molar ratio as shown in Figure 9. In classical free-radical copolymerization of St and MAH, reaction rate, K_p , was shown to decrease when the initial proportion of styrene increased,¹⁷ which was in agreement with our experimental results. The molecular weights of the copolymer showed negligible change.

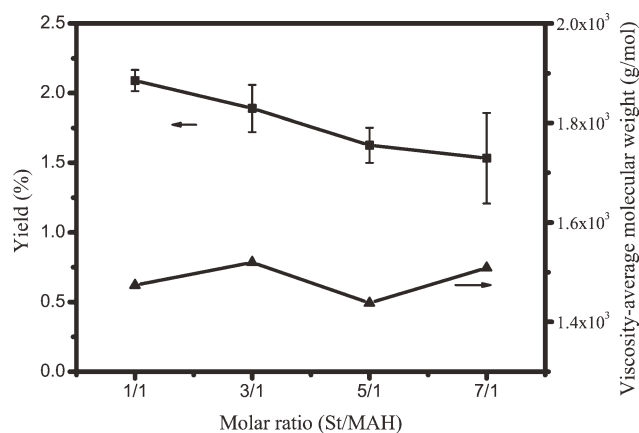


Figure 9 Effects of molar ratio on yield and viscosity average molecular weight. (Discharge power: 20 W; initiation time: 30 min; CO₂ flow rate: 80 mL/min; postpolymerization time: 1 h; polymerization temperature: 303 K).

DISCUSSION

In these experiments, when the free-radical catching agent, DPPH, was added to the polymerization system, no product was obtained. We deduced that the plasma copolymerization in the present study followed the free radical polymerization mechanism.¹ The mechanism by which the initiator generated free radicals was still unknown.

It was well known that St was inert to initiation by plasma which was also found in our experiment, but with the addition of MAH, the reaction was accelerated. The active species produced in the vapor space by a radio-frequency discharge were initially believed to be the initiator of plasma polymerization.¹⁻⁹ But in remote plasma initiation, the ions lost energy due to the collisions with the other objects in the reactor and tube when they traveled some distance from the source.^{18,19} Therefore, only the active groups such as excited CO₂, O₂, O atoms, and other free radicals, which can live longer across the distance to the solution, would result in the formation of MAH radical sites, which was prerequisite for the proposed stabilization of the styryl radical reaction intermediate.²⁰

CONCLUSIONS

Plasma-initiated polymerization was carried out at an ambient temperature and pressure using DBD technology. The SMA was shown by ¹H and

¹³C-NMR spectra to have a dominant alternating structure with little randomness. The plasma-initiated polymerization in this experiment was shown to have followed the free-radical polymerization mechanism. The yield of SMA increased with the increase of initiation time and polymerization temperature, remained unchanged with the increase of flow rate, and decreased rapidly with the increasing of St-MAH molar ratio. It was proven that the active species of the plasma could initiate the polymerization continually. The yield of SMA did not increase with the addition of postpolymerization time due to the embedding of residual radicals. It suggested that a good solvent was needed in PIP to prepare a high molecular weight polymer.

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