MONOMER REACTIVITY RATIO AND THERMAL PERFORMANCE OF α-METHYL STYRENE AND GLYCIDYL METHACRYLATE COPOLYMERS

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Abstract Synthesis and characterization of the copolymers (PAG) of α-methyl styrene (AMS) and glycidyl methacrylate (GMA) are presented. The copolymers of PAG were characterized by gel permeation chromatography (GPC), Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (^{1}H-NMR) and thermogravimetry (TG). Based on the copolymer compositions determined by ^{1}H-NMR, the reactivity ratios of AMS and GMA were found to be 0.105 ± 0.012 and 0.883 ± 0.046 respectively by Kelen-Tüdös method. TG revealed that thermal stability of the copolymers decreased with increasing the AMS content in the copolymers, which indicated that the degradation was mainly caused by the chain scission of AMS-containing structures. Under heating, the copolymers depolymerize at their weak bonds and form chain radicals, which could further initiate other chemical reactions.

Keywords: Copolymerization; α-Methyl styrene; Glycidyl methacrylate; Reactivity ratios; Depolymerization.

INTRODUCTION

α-Methylstyrene (AMS) has a relatively low ceiling temperature (61°C), above which significant depropagation of the resulting polymer is expected[1]. The monomer, AMS, is a main byproduct of the large-scale manufacture of phenol and acetone using low-cost cumene (isopropyl-benzene), and good yields of this monomer can be obtained from cumene by dehydrogenation. But this monomer has not gained extensive applications in industry because of its low reaction activation.

Though homopolymerization of AMS is not possible at temperatures higher than 61°C. Copolymerization, however, can and does proceed. Also, copolymerization is an effective route to combine the excellent performance of two homopolymers from the two corresponding monomers. Many investigators have studied the copolymerization of AMS with various monomers[2–7].

Herein, we report the synthesis of the copolymers of glycidyl methacrylate (GMA) and AMS with various contents of AMS in the resulting copolymers, and the reactivity ratio of AMS with GMA at 65°C under low conversion (< 10%) was calculated by Kelen-Tüdös method for the first time. The obtained copolymers can be used as *in situ* compatibilizer in the blends of PP and other components (*i.e.* PA6, PA66 and so on)[8]. Moreover, they can be used as macroinitiator in the copolymerization reactions of various systems, which will be reported in the subsequent papers of our laboratory. This is believed to be widely valuable in polymerization field and will expand greatly the applications of AMS in industry.

Copolymers containing GMA and AMS as monomeric units can be represented as Scheme 1.
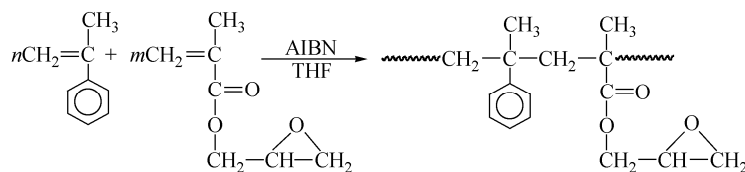
Scheme 1 Synthesis and structure of copoly(AMS-GMA)

EXPERIMENTAL

Materials

Glycidyl methacrylate (GMA), Beijing Yanshan Petrochemical Chemical Plant (China) (98%, purity), was used without further purification. α-Metyl styrene (AMS, Tongji University, Shanghai, China) was distilled under reduced pressure to exclude the impurities. 2,2'-Azobisisobutyronitrile (AIBN) was recrystallized from ethanol, dried under vacuum at room temperature and stored in a desiccator in advance. Tetrahydrofuran (THF), acetone and methanol (Beijing Yili Chemical Regent Co., China) were all used as received.

Synthesis of Copolymers

Synthesis of the copolymers of PAG was carried out in a typical procedure as described below. A certain amount of AMS, GMA and AIBN was added to THF in a four-necked flask. After dissolution, the solution was degassed with N_2 for 20 min to exclude the O_2 dissolved in the solution. Then, the flask containing the reaction solution was placed in a water bath of a predetermined temperature. After polymerization for a certain time, the resulting copolymers were precipitated from methanol and filtered off. The copolymers were dissolved in acetone and then precipitated with methanol three times for purification. Lastly, the copolymers were dried under vacuum at 50°C.

Copolymer Characterization

IR spectra of the copolymers were recorded with a Nicolet Nexus-670 FT-IR spectrophotometer on solid samples as KBr pellets. The copolymer compositions were determined by quantitative ^{1}H-NMR using a Bruker av600 (600 MHz) spectrometer at room temperature. Deuteroacetone was used as solvent and TMS as internal standard, respectively. The methoxy resonance patterns were evaluated according to the reported literatures[9]. Resonance areas were determined by using a planimetry. The molecular weights and their polydispersity were determined by using a Waters 515–2410 gel permeation chromatograph (GPC), with tetrahydrofuran as eluent and polystyrene standards for calibration. Thermogravimetric analysis (TGA) was conducted using a Netzsch TG209 TG analyzer under a nitrogen atmosphere. The dried copolymers were heated from 50°C to 600°C with a heating rate of 10 K/min.

To study the depolymerization of PAG, we designed specially a group of experiments. About 0.1 g copolymers were fed into tubes, and O_2 was removed by N_2 purging for 20 min prior to the tubes being submerged into a oil bath, which was kept at a predetermined temperature (190°C). After depolymerization, the tubes were took out and then put into ice-water mixture to stop the depolymerization reaction.

RESULTS AND DISCUSSION

Evolution of Copolymerization

With the total monomer concentration and other reaction conditions being kept as the same, the effects of monomer composition on the copolymerization are presented in Table 1. It was found that different monomer compositions had pronounced influence on the copolymerization. The lower AMS feed ratio leads to higher molecular weights and higher monomer conversion as well. It appears obviously that AMS is the main factor in reducing the degree of polymerization and the molecular weights. This suggests that AMS can modify the kinetics of copolymerization reactions by sharply reducing the rate of polymerization at relatively low concentrations in the feed. And this result agrees well with the fact that AMS undergoes radical-initiated homopolymerization with much difficulty.

Table 1. Effects of monomer composition on copolymerization of AMS and GMA[a]

[AMS]/[GMA] (mol/mol)	C (%)	PAG			
		$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n	AMS content (mol%)[b]
1/2	1.61	4.57	6.19	1.31	25.60
1/5	2.75	5.71	8.12	1.42	11.00
1/10	11.07	12.18	19.28	1.57	7.42
1/20	20.23	21.00	36.87	1.63	3.56

[a][AIBN] = 0.1 wt%, T = 65°C, t = 7.5 h, [AMS] + [GMA] = 25 wt%
[b]Values measured by ^{1}H-NMR, referenced to tetramethyl silicane (TMS)

The influence of reaction time and reaction temperature on the copolymerization is described in Fig. 1. It was found from that the monomer conversion increased with increasing the reaction time and reaction temperature. The results indicate that the copolymerization of AMS and GMA follows well the general free radical copolymerization, which suggests the depolymerization reaction can be neglected under the reaction conditions (50−65°C).
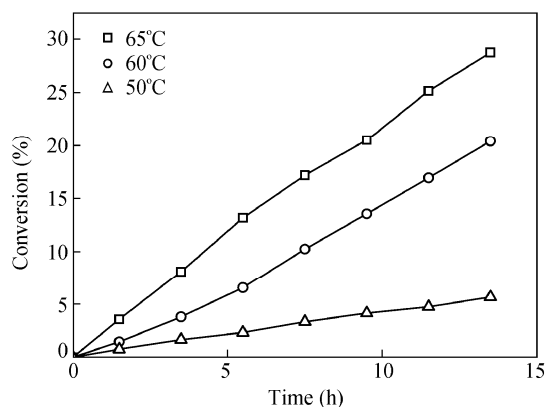
Fig. 1 Effect of reaction time and reaction temperature on monomer conversion
[AIBN] = 4 wt%; T = 65°C; [M] = 25 wt%; [AMS]/[GMA] (mol/mol) = 1:2

Effects of some other factors, such as monomer concentration and initiator concentration have also been studied. In most cases, low molecular weight is a characteristic feature of this reaction system.

Characterization of the Copolymers
A typical infrared spectrum from 4000 cm^{-1} to 400 cm^{-1} for one of the PAG copolymers is presented in Fig. 2. The C−H stretching vibrations of methyl (CH$_3$), methylene (CH$_2$) and methine groups (CH) of AMS and GMA appeared at 2996.15 and 2940.77 cm^{-1}, respectively. The characteristic absorption bands of ester carbonyl groups of the copolymer are observed at 1729.23 cm^{-1}. The C−H bending vibrations of α-methyl groups of
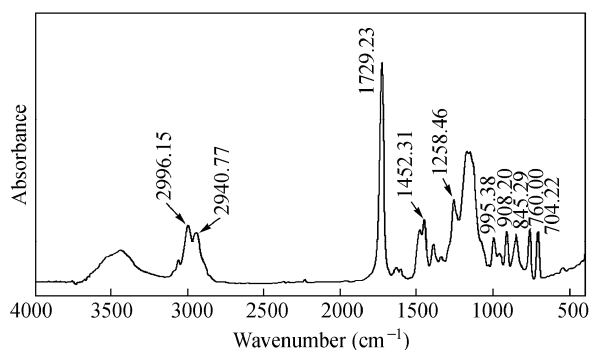
Fig. 2 FT-IR spectrum of a PAG copolymer (AMS = 8.82 mol%)

GMA units appear at 1452.31 cm^{-1} as a sharp band. In addition to this, a sharp band at 908.20 cm^{-1} which is due to the epoxy groups of GMA units indicates that the polymerization proceeds through acrylic double bonds. Also a band at 704.22 cm^{-1} can be seen which is attributed to C$-$H vibrations of aromatic groups of AMS.

The ^{1}H-NMR spectrum of a PAG copolymer (AMS = 8.82 mol%) is shown in our previous paper[8]. The aromatic protons show signals between $\delta = 7.31$ and 6.92, which are attributed to phenyl groups of AMS units. The spectrum shows two signals at $\delta = 4.33$ and 3.75 due to the splitting of methylene protons attached to the ester group of the GMA unit. The peak at $\delta = 3.16$ is due to the methine proton of the epoxy group. The methylene protons of the epoxy group show signals at $\delta = 2.78$ and 2.51. The methylene group of the polymer backbone shows a broad signal between $\delta = 2.45$ and 1.55 due to tacticity. The α-methyl protons of both monomeric units show signals between $\delta = 1.55$ and 0.82.

Reactivity of AMS and GMA

The chemical composition of the copolymers depends on the relative reactivity between the two monomers. Monomer reactivity ratios are important for quantitatively predicting the copolymer composition for any starting feed and for understanding the kinetic and mechanistic aspects of copolymerization. In this work, the compositions of A/G copolymers were quantitatively determined from the corresponding ^{1}H-NMR spectra of copolymer samples prepared with different monomer feeds. The compositions of the resulting copolymers are list in Table 2, with the mole fraction of AMS in feed varied from 0.0476–0.5.

Table 2. Feed ratio and copolymer composition

f_1	0.5	0.3333	0.1667	0.0909	0.0476
F_{1E}	0.4014	0.3051	0.1816	0.1091	0.0607
F_{1T}	0.4287	0.3186	0.1611	0.0882	0.0511

f_1 is the mole fraction of AMS in feed composition;
F_{1E} is the mole fraction of AMS in copolymer composition calculated from equation (5);
F_{1T} is the mole fraction of AMS in copolymer composition determined from ^{1}H-NMR spectroscopy.

The copolymer composition data were used to determine the terminal model reactivity ratio (KT method). Since the peak intensity corresponds to the total number of protons of a particular group, the mole fractions of AMS or GMA were calculated by comparing the intensities of well separated aromatic protons of AMS units and methylene protons attached to $-$COO$-$ of GMA units by the following equation:

$$\text{Mole percent of AMS in copolymer (\%)} = \frac{A/5}{A/5 + B/2} \times 100\% \tag{1}$$

Where A is the integrated peak areas of aromatic protons ($\delta = 7$–8) of AMS units in ^{1}H-NMR spectroscopy; B is the integrated peak areas of methylene protons signals attached to $-$COO$-$ of GMA units in ^{1}H-NMR spectroscopy ($\delta = 4.25$–4.30, and $\delta = 3.70$–3.80, respectively).

Number 5 expresses that there are five aromatic protons in AMS; and 2 denotes that there are two methylene protons attached to $-$COO$-$ of GMA.

From Table 3, we can see that the parameters Q and e of the Alfrey-Price equation[10] are 0.98 and -1.27 for GMA and 0.96 and 0.20 for AMS, respectively[11].

Table 3. Q and e value of GMA and AMS

Monomers	Q	e
AMS	0.98	-1.27
GMA	0.96	0.20

According to Alfrey-Price, the relationship of Q-e is as follows:

$$r_1 = Q_1/Q_2 \exp[-e_1(e_1 - e_2)] \tag{2}$$

$$r_2 = Q_2/Q_1 \exp[-e_2(e_2 - e_1)] \tag{3}$$

$$r_1 r_2 = \exp[-(e_1 - e_2)^2] \tag{4}$$

It is estimated that the reactivity ratio are $r_1 = 0.16$ (AMS), $r_2 = 0.73$ (GMA), $r_1 r_2 = 0.115$, respectively.

Then, the value of r_1 and r_2 is substituted into differential equation with regard to copolymerization composition:

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \tag{5}$$

The molar ratio of AMS in copolymer composition (that is F_{1E}) is calculated and listed in Table 2 together with the true values determined from the corresponding ^{1}H-NMR spectra of copolymer samples and the molar fractions of monomers in feed, where f_1 is the mole fraction of AMS in feed composition, F_{1E} is the mole fraction of AMS in copolymer composition calculated from Eq. (5), and F_{1T} is the mole fraction of AMS in copolymer composition determined from ^{1}H-NMR spectroscopy.

Also, it is calculated that $\left| \dfrac{F_{1E} - F_{1T}}{F_{1E}} \right| \times 100\%$ ranges from 4% to 20%.

As early as 1970 s, Kelen and Tüdös have proposed a simple graphically evaluable linear method for the determination of r_1 and r_2, the monomer reactivity ratios in copolymerization[12]. The Kelen-Tüdös equation is as follows:

$$\eta = (r_1 + \frac{r_2}{\alpha}) \xi - \frac{r_2}{\alpha} \tag{6}$$

where α is a suitably chosen parameter, and η and ξ are variables obtained from the charge and copolymer composition; $\eta = \dfrac{G}{\alpha + F}$, $\xi = \dfrac{F}{\alpha + F}$, $\alpha = \sqrt{F_{min} \times F_{max}}$, $G = \dfrac{x(y-1)}{y}$, $F = \dfrac{x^2}{y}$, $x = \dfrac{M_1}{M_2}$, $y = \dfrac{dM_1}{dM_2}$; M_1 is the mole fraction of AMS in feed; M_2 is the mole fraction of GMA in feed; dM_1 is the mole fraction of AMS in copolymer; dM_2 is the mole fraction of GMA in copolymer; F_{min} and F_{max} are the lowest and highest from the experimental data, and the values corresponding to the parameters are listed in Table 4.

Table 4. Composition data and K-T parameters for the copolymerization of AMS (1) with GMA (2) in THF solution at 65°C[a]

Sample	C (%)	x	y	G	F	η	ξ
1	0.21	2.97	1.1496	0.3865	7.6730	0.0452	0.8979
2	1.15	2.01	0.8539	−0.3439	4.7314	−0.0614	0.8442
3	2.48	1.01	0.5652	−0.7769	1.8048	−0.2901	0.6740
4	3.84	0.50	0.3441	−0.9531	0.7265	−0.5959	0.4542
5	6.04	0.21	0.2028	−0.8255	0.2175	−0.7571	0.1995
6	8.48	0.13	0.1236	−0.9218	0.1367	−0.9130	0.1354
7	9.14	0.11	0.1219	−0.7924	0.0993	−0.8151	0.1021

[a] $\alpha = 0.8729$

By plotting η versus ξ according to the linear Eq. (6) (Fig. 3), we can obtain directly r_2 (i.e., r_2/α) and r_1 from the intercepts at $\xi = 0$ and $\xi = 1$, respectively, that is, $r_1 = 0.105 \pm 0.012$, $r_2 = 0.883 \pm 0.046$. The values of r_1 and r_2 are all less than 1, which are accordant with those calculated according to Q-e method (Eq. (6)) described above. The fact of the value of r_1 being less than r_2 suggests that the system leads to random distribution with longer sequence of GMA units in the copolymer chain.
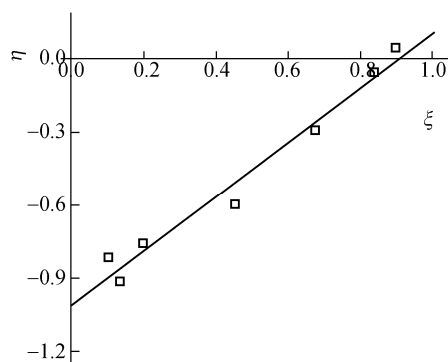
Fig. 3 Kelen-Tüdös plot for the AMS and GMA copolymer system

Figure 4 shows composition data (mole fraction AMS in the copolymers versus mole fraction in the feed) for the copolymers obtained at 65°C. The plot shows that the mole fraction of AMS in the copolymers increases with increasing the level of AMS in the feed. As the mole fraction of AMS in the feed increases to the limiting level of about 0.75 (under the present reaction conditions), the mole fraction of AMS in copolymers reaches a maximum level exceeding 0.5. This to some degree indicates that there are AMS-AMS chain segments in the copolymers.
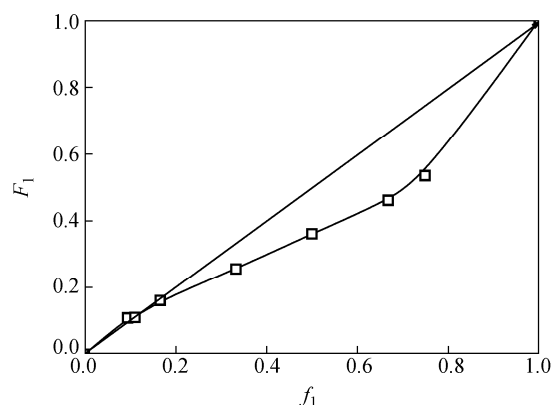

Fig. 4 Feed ratio versus copolymer composition curves of PAG

Thermogravimetric Analysis

Thermogravimetric analysis (Table 5) was employed in estimating the percent weight loss of the copolymers which undergo decomposition. Thermogravimetric analysis (TGA) curves for PAG are shown in Fig. 5. Figure 5 shows that the thermal degradation of PAG proceeds in two steps. In the first, degradation mainly starts at the weak parts, *i.e.*, the unsaturated chain ends or the weak bonds, and the second stage is resulted from random chain scission at higher temperatures. Plots of T_0 (temperature where degradation starts), T_{50} (temperature with 50% weight left) and T_5 (temperature with 5% weight left) obtained from TG data are shown in Table 5. T_0 indicates that the initial degradation temperature of the copolymers almost remains at the same temperature (60–80°C), which stems from the depolymerization of AMS sections in the copolymers. T_{50} shows a substantial increase when the content of AMS in the monomer ratio decreases (the charge ratio less than 1/5), indicating the degradation during this stage is mainly caused by the chain scission of AMS-containing structures. However, T_{50} changes little with the further decrease in AMS content in the copolymers. But for T_5, it exhibits slight changes for all the copolymers. Also, it should be pointed out that, when temperature rises to 350°C, the copolymers with varied AMS contents differ slightly in their thermal degradation. This demonstrates that at such a high temperature, the copolymers undergo random decomposition, irrespective of the AMS content in the copolymer.

This is different from the thermal degradation behavior of the copolymers at low temperatures, as discussed above. In conclusion, TGA results indicate clearly that the thermal stability of the copolymers decreases with increasing the AMS content in the copolymer.

Table 5. Thermogravimetric analysis of the copolymers

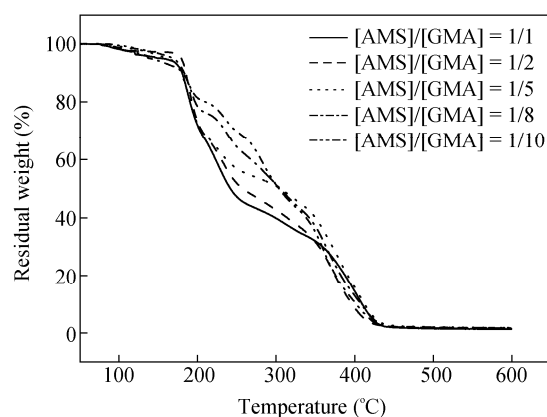| [AMS]/[GMA][a] (mol/mol)	1/1	1/2	1/5	1/8	1/10
T_0 (°C)	63.8	74.4	62.8	72.5	79.7
T_{50} (°C)	241.8	256.7	305.0	304.9	303.5
T_5 (°C)	422.4	412.8	426.6	423.8	419.1

[a] Refer to the feed ratio

Fig. 5 TGA plots of the copolymers

Depolymerization of the Copolymers

The relevant results were presented in Table 6. From Table 6, we can see obviously that the molecular weights of the copolymers decrease with the increase of heating time, while the polydispersity increases at the same time. This result confirms intensively the occurrence of the depolymerization of the copolymers at this heating temperature.

Table 6. The molecular weights of the copolymers versus heating time (AMS = 25.6 mol%)

Heating time (min)	$M_n \times 10^{-3}$	$M_w \times 10^{-3}$	M_w/M_n
0	2.05	2.73	1.33
5	1.21	2.24	1.84
10	1.17	2.20	1.88
15	1.15	2.18	1.90
20	1.03	2.09	2.02
25	0.97	2.08	2.16

Solubility of the Copolymers

The solubility of the copolymers was tested in some common solvents. The results indicate that the copolymers were soluble in chloroform, acetone, dimethyl acetamide, dimethyl formamide, tetrahydrofuran, benzene, toluene and xylene, but insoluble in *n*-hexane and hydroxyl group containing solvents such as methanol and ethanol.

CONCLUSIONS

The copolymers of GMA and AMS can be synthesized via free radical solution polymerization. From the results of the investigation, it can be concluded that the monomer conversion and the molecular weights of the copolymers are affected greatly by reaction conditions, *i.e.*, monomer composition, monomer concentration and initiator concentration. Based on the copolymer compositions determined by ^{1}H-NMR, the reactivity ratios are calculated by Kelen-Tüdös method and found to be $r_1 = 0.105 \pm 0.012$ (AMS), $r_2 = 0.883 \pm 0.046$ (GMA),

respectively. The thermal analysis results reveal that the thermal stability of the copolymer decreases with increasing the AMS content in the copolymer, and the decrease of the molecular weights of the copolymers with the increase of heating time confirms the existence of depolymerization of the copolymers. These unique characteristics are expected to be applied to many well designed applications.

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