Synthesis of Glutarimides from PMMA Copolymers, Part 3: Use of Functional Amines

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ABSTRACT: Imidization reactions onto PMMA copolymers were performed in the presence of primary amines. This study allowed establishing a correlation between the functional group of the primary amine and the reactivity of the primary amine toward ester groups of PMMA. This correlation was allowed by using model PMMA/PMAA copolymers, i.e., obtained using a chain transfer agent by radical polymerization. According to the suggested mechanism of PMMA imidization, methylamine afforded higher content of glutarimide groups, hence leading to high T_g values of about 160°C. The use of bulky groups for the primary amine instead, i.e., cyclohexyl, decreased the content of glutarimide function. Thermogravimetric analysis revealed a high thermostability of imidized PMMA with a starting degradation temperature of about 400°C, also dependant of the amine functional group. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 118: 1867–1871, 2010

Key words: polyimides; copolymerization; thermal properties; functionalization of polymers; glass transition

INTRODUCTION

Methacrylic polymers are widely used for several applications, thanks to their properties of excellent transparency, their good resistance to aging or corrosion and their good thermoforming ability. However, some applications require high T_g and high thermal stability, then methacrylic polymers cannot compete with polycarbonate polymers, although these polymers have a rather high manufacturing cost. The aim of this article is to propose modified methacrylic polymers having both high T_g and thermal resistance obtained with reduced manufacturing cost. Numerous processes have been used to chemically modify methacrylic polymers, and especially PMMA.[1–6] Most of them consist on creating a cyclic structure on the main chain, leading to increased chain stiffness. The cyclic structure can be obtained either by postpolymerization chemical modification, i.e., anhydride or glutarimide groups, or during the MMA polymerization with cyclic comonomers, i.e., maleic anhydride. The probably most efficient technique, in the way of increasing the PMMA T_g, is based on the PMMA ester group cyclization,[7] leading to cyclic imides along the polymer backbone, i.e., the polyglutarimide type compounds. This cyclic structure allows creating internal strain, which increases chain stiffness and also the T_g. From economical point of view, this technique seems the most interesting and has been developed by the Rohm and Haas company to lead to glutarimides compounds sold under the Kamax® trade name.[8–10] These compounds are obtained through imidization of PMMA by aminolysis in a solvent medium and presents high T_g values of about 200°C. The mechanism consists on the N-alkylation reaction of PMMA as the first step, followed by amidization reaction in the presence of a primary amine. The resulting amide-acid intermediate leads to N-methyl glutarimide by cyclodehydratation. In previous articles,[11–13] we have performed kinetics of PMMA aminolysis in the presence of methylamine, by means of FTIR and showed that the content of functional groups (imide, acid, and ester) was dependent on both the temperature and reaction time. Noteworthy, the highest content of imide group was 50 mol % at 250°C after 6 h of reaction, although the acid content remained as low as 10 mol %. To our knowledge, however the functional R group of the primary amine was not considered to potentially increase the imidization content of PMMA. In this article, we investigate the imidization reaction as a function of the primary amine, to target a high content of imide group (higher than 50 mol%) while keeping constant the acid group content (about 10 mol%). The presence of imide group in the polymer structure increases the thermal stability.[14] Thus, imidization in the presence of functional primary amines will allow incorporating functional groups onto PMMA.
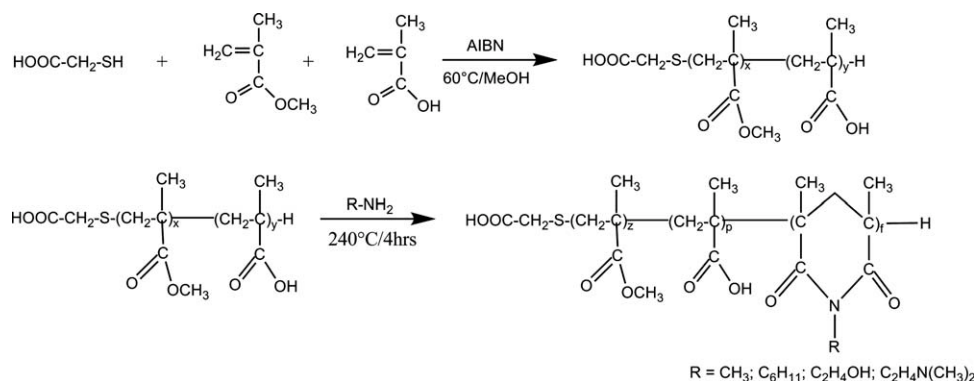

Figure 1 Synthesis of glutarimide polymers using different primary amines following a two-steps reaction.

EXPERIMENTAL PART

Materials

All chemicals were purchased from Aldrich and used without further purification. AIBN was re-cristallyzed into methanol.

Measurements

The chemical structure of the products was determined by ^1H and ^{13}C NMR (Bruker AC 400 MHz) at room temperature in CDCl$_3$ solutions. S, d, t, q, m abbreviations stand for singlet, doublet, triplet, quadruplet, and multiplet, respectively. The INVGATE procedure with delay D1 of 10 s was used to quantify the final yield. Infrared (FTIR) spectra were recorded on a Nicolet 510P FTIR spectrometer with a band accuracy of ± 4 cm^{-1}. Thermogravimetric analyses (TGA) were performed with a TGA/SDTA 851 thermobalance from Mettler DAL 75965 and Lauda RC6 CS cryostat apparatus in static air with a heating rate of 10°C min^{-1} from room temperature up to a maximum of 600°C. Differential scanning calorimetry (DSC) measurements were conducted using a TA2920 analyser from TA Instruments DA 73085, an RCS DA cooler and Sartorius MC5 balance. Scans were recorded at a heating/cooling rate of 20°C min^{-1} from 0 to 250°C.

Synthesis of MMA/MAA copolymers

A total of 10 g of methylmethacrylate (MMA) (0.10 mol), 10.5 g of methylmethacrylic acid (MAA) (0.122 mol), 0.13 g of thioglycolic acid TGA (1.4 10^{-3} mol), 0.36 g of AIBN (2.1 10^{-3} mol), and 80 g of methanol were introduced in a round bottom flask, equipped with a condenser, and stirred at 80°C for 6 h. The final product was purified by vacuum distillation, and precipitated in acetonitrile. The copolymer was obtained with 87% yield.

^1H NMR (DMSO): $\delta = 1$ ppm (6H, C—CH$_3$), $\delta = 3.1$ ppm (2H, HOOC—CH$_2$—S—), $\delta = 1.8$ ppm (4H, —CH$_2$—C—CH$_2$—C), $\delta = 3.6$ ppm (3H, —C—COOCH$_3$), $\delta = 12.3$ ppm (1H, —C—COOH).

Imidization of MMA/MAA copolymers

A solution of 10 g of MMA/MAA copolymer (0.107 mol) and 10 g of methanol is introduced in a two-necked round bottom flask. Then, 11 g of methylamine (0.13 mol) are added dropwise at room temperature and the solution is stirred for 30 min. The excess of both amine and methanol are evaporated and the salt is obtained by precipitation in acetonitrile. A sum of 10 g of salt and 10 g of methanol are then introduced in the autoclave and the solution is stirred at 230°C for 4 h. After cooling, the final product is obtained by precipitation in diethylether.

TABLE I
Characteristics of Different MMA/MAA Copolymers Obtained by Conventional Radical Polymerization

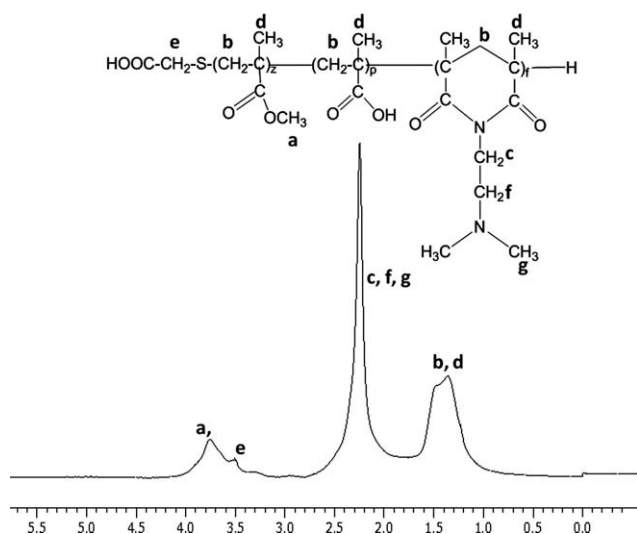| Copolymer | MMA/MAA content (mol %) | | Yield (w %) | Molecular weight (g/mol) | | T_g (°C) |
	Initial feed	Composition		Theoretical	Experimental	
MMA/MAA 31	50/50	57/43	48	3700	3100	118
MMA/MAA 29	40/60	54/46	70	2700	2900	115
MMA/MAA 24	44/56	61/39	84	2700	2400	110
MMA/MAA 11	30/70	45/55	68	1600	1100	105
MMA/MAA 186	40/60	50/50	86	20000	18600	160

Figure 2 ^{1}H NMR spectra of MMA/MAA copolymer (upper spectrum) and MMA/MAA copolymer imidized with N,N-dimethylethylenediamine (below spectrum).

Imidization with methylamine

^{1}H NMR (D$_2$O): δ = 0.8–2.2 ppm (—CH$_2$— and —CH$_3$), δ = 2.9 ppm (3H, N—CH$_3$), δ = 3.6 ppm (3H, —C—COOCH$_3$).

Imidization with cyclohexylamine

^{1}H NMR (D$_2$O): δ = 0.8–2.2 ppm (—CH$_2$— and —CH$_3$), δ = 3.6 ppm (3H, —C—COOCH$_3$), δ = 4.4 ppm (1H, cyclohexyl group), δ = 0.9 ppm (10H, cyclohexyl group).

Imidization with ethanolamine

^{1}H NMR (D$_2$O): δ = 0.8–2.2 ppm (—CH$_2$— and —CH$_3$), δ = 3.6 ppm (3H, —C—COOCH$_3$), δ = 2.8 ppm (2H, —N—CH$_2$CH$_2$OH), δ = 3.6 ppm (2H, —CH$_2$CH$_2$OH), δ = 2.8 ppm (1H, —CH$_2$CH$_2$OH).

Imidization with N,N-dimethylethylenediamine

^{1}H NMR (D$_2$O): δ = 1–1.8 ppm (—CH$_2$— and —CH$_3$), δ = 3.6 ppm (3H, —C—COOCH$_3$), δ = 2.3 ppm (10H, —N—CH$_2$CH$_2$N(CH$_3$)$_2$)$_3$.

RESULTS AND DISCUSSION

Imidization using different primary amines

As already discussed in the introduction, imidization of PMMA polymers consists on the N-alkylation reaction of PMMA as the first step, leading to poly (methyl methacrylate-co-methacrylic acid) intermediate followed by its imidization reaction in the presence of a primary amine. To avoid the first step, MMA/MAA copolymers can be directly synthesized by conventional radical copolymerization, leading to statistical copolymers. Radical copolymerizations of MMA/MAA usually lead to high molecular weight copolymers, then the resulting copolymers are hardly soluble in common organic solvents and imidization becomes challenging. Low molecular weights MMA/MAA copolymers can be reached by using free radical chain transfer, i.e., in the presence of a chain transfer agent. A series of 5 MMA/MAA copolymers was synthesized at 60°C using thioglycolic acid (Fig. 1) as chain transfer agent[15,16] and low molecular weight (Mw) copolymers were obtained ranging from 1000 to 20,000 g/mol (Table I). Targeting low Mw values has two aims: these copolymers can be used as model compounds to perform imidization reactions; low Mw copolymers remain soluble in common organic solvents enabling chemical modifications. Glass transitions (T_g) are also reported in Table I ranging from 105 to 160°C, depending on the copolymer Mw values. The five MMA/MAA copolymers were characterized by means of ^{1}H NMR, allowing establishing the final molar composition of MMA and MAA for each copolymer (Table I). A similar characterization, i.e., ^{1}H NMR and IRTF, was added in the Supporting Information when the copolymers were imidized by using methylamine.

From each MMA/MAA copolymers imidization reactions were performed at 230°C during 4 h (Fig. 1). All the imidized copolymers were characterized by ^{1}H NMR analysis (Fig. 2), which allows for evaluating the molar content of each functional

TABLE II
Glutarimide Content and T_g Values of MMA/MAA Copolymers Imidized Using Different Primary Amines

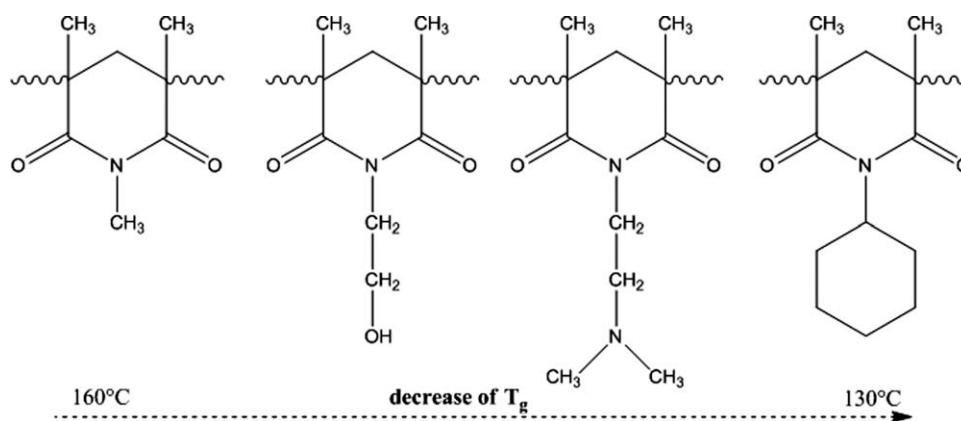| Copolymer	Amine	MMA/MAA/GluI content (mol %)			T_g (°C)
		MMA	MAA	GluI	
MMA/MAA 31	CH$_3$—NH$_2$	17	17	66	160
	C$_6$H$_{11}$—NH$_2$	27	8	65	130
	HO—C$_2$H$_4$—NH$_2$	30	20	50	138
	(CH$_3$)$_2$—N—C$_2$H$_4$—NH$_2$	28	22	50	130
MMA/MAA 24	CH$_3$—NH$_2$	24	18	58	150
	HO—C$_2$H$_4$—NH$_2$	31	18	51	138
MMA/MAA 186	CH$_3$—NH$_2$	29	10	61	162

Figure 3 T_g values of imidized PMMA as a function of the functional amines.

group, i.e., MMA, MAA, and glutarimide (GluI). The results are reported in Table II as a function of both the Mw and of the primary amine. Considering methylamine, we can note that the MMA/MAA/ GluI contents are not influenced by the Mw values of the copolymers. The glutarimide (GluI) content is ranging from 50 to 66 mol % and is directly related to the type of primary amine. Indeed, imidization reactions in the presence of methylamine afford the highest GluI molar content; whereas we were only enable to reach 50 mol % of GluI by using *N,N*-dimethylethylenediamine as primary amine. This result may be ascribed to the steric hindrance of *N,N*-dimethylethylenediamine compared to methylamine. Noteworthy, imidization with cyclohexylamine led to similar glutarimide content compared to methylamine and even higher than ethanolamine; the high reactivity of cyclohexylamine toward PMMA was already observed by Legay et al.[11] Cyclohexylamine is also very interesting reagent to manipulate as it is a liquid at room temperature, facilitating the reaction processing. However, due to the steric hindrance of the cycloaliphatic group, lower T_g were obtained compared to those observed with methylamine. For instance, imidization of MMA/MAA 31 (showing a T_g value of 118°C) in the presence of methylamine leads to poly(methacrylic-*co*-glutarimide) with T_g value of 160°C, whereas a T_g value of 130°C is observed when imidization occurs with cyclohexylamine. Finally, for the same level of glutarimide groups, a correlation may be drawn between the functional groups of primary amines and of the T_g values (Fig. 3). As expected, the bulkier functional group will lead to lower T_g values. One may note that hydroxyl groups afford higher T_g values, compared to *N,N*-dimethylethylenediamine, which may be probably ascribed to hydrogen bonding in between PMMA chains.

We can also note that the methacrylic acid molar content is between 10 to 20 mol % whatever the type of primary amine used for the imidization reaction.

This molar content will approximately correspond to that of the incorporated methacrylic double bond allowing further crosslinking reaction through UV-photopolymerization. Finally, the thermostability of poly(methacrylic-*co*-glutarimide) copolymers was evaluated as a function of the primary amine type (Fig. 4). First of all, imidization of polymethacrylic copolymers always increases the thermostability, as expected, to reach a starting degradation after 400°C for methylamine. Two behaviors are also distinctively observed related to the type of primary amine, when methylamine or ethanolamine are the amine reagents poly(methacrylic-*co*-glutarimide) copolymers show a starting degradation occurring at high temperature. In the case of cyclohexylamine and of *N,N*-dimethylethylenediamine, a first degradation occurs at about 150°C, attributed to the loss of the amine functional group, i.e., cyclohexyl.
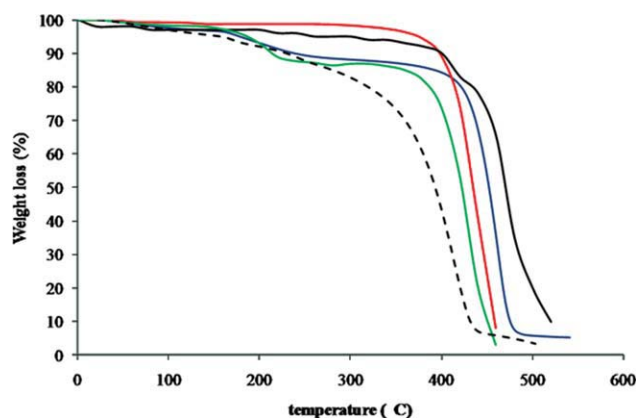

Figure 4 Thermostability of poly(methacrylic-*co*-glutarimide) copolymers obtained using methylamine (red curve), ethanolamine (black curve), *N,N*-dimethylethylenediamine (blue curve), and cyclohexylamine (green curve). The thermostability of the equivalent MMA/MAA copolymer is also given (dash line). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
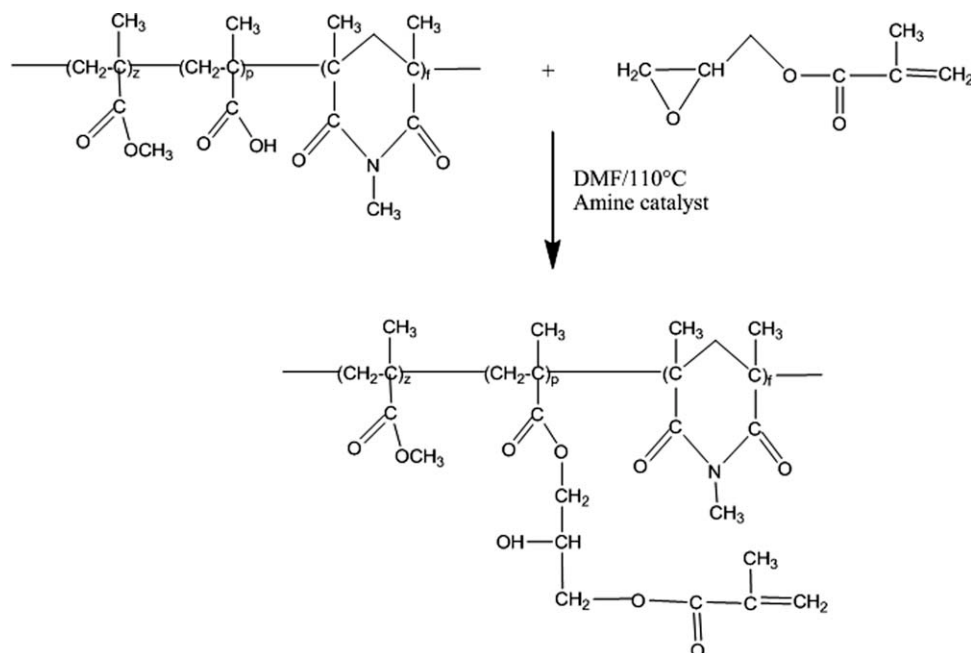
Figure 5 Methacrylation of poly(methacrylic-*co*-glutarimide) by epoxy-acid reaction.

Methacrylation of poly(methacrylic-*co*-glutarimide)

Considering both thermostability and T_g measurements, imidization of MMA/MAA 186, i.e., of 18,600 g/mol, was performed using methylamine (Table II) leading to about 60 mol % of glutarimide content and about 10 mol % of remaining methacrylic group. The acid groups were reacted with glycidyl-methacrylate at 110°C in DMF using *N,N*-dimethyl-dodecylamine as catalyst (Fig. 5) to incorporate a methacrylic double bond allowing further UV-photo-polymerization. Ionol compound was also added to avoid any radical polymerization of glycidylmeth-acrylate. ^{1}H NMR of the purified product showed that methacrylation proceeded quantitatively. We can also remark that the T_g value was decreased to 140°C due to the steric hindrance of the methacrylic double bond.

CONCLUSION

In this third article on imidized PMMA, we have obtained a new generation of imidized PMMA by imidization of ester groups in the presence of different primary amines. High T_g values (up to 160°C) could be reached, corresponding to a high molar content of glutarimide groups (about 60%) obtained with methylamine. The model study of PMMA imidification allowed drawing a reactivity order of primary amines (toward PMMA) according to their functional groups. As expected, bulky groups led to imidized PMMA with the lower T_g values and with the lower contents of glutarimides groups. Metha-crylation of imidized PMMA was obtained by using the remaining methacrylic functions and the resulting modified polymers will be, in a forthcoming article, crosslinked by UV-photopolymerization and their thermal stability and their mechanical properties will be studied.

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