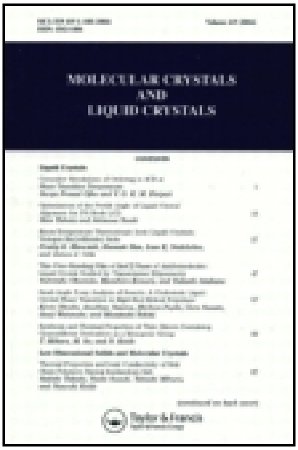

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Effect of Glass Transition Temperature on Compression and Elastic Properties of Poly(Meth)Acrylate Copolymer Thin Films and their Photoresist Patterns

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Version of record first published: 12 Mar 2007

To cite this article: Heon Seung Chae & Yun Heum Park (2007): Effect of Glass Transition Temperature on Compression and Elastic Properties of Poly(Meth)Acrylate Copolymer Thin Films and their Photoresist Patterns, Molecular Crystals and Liquid Crystals, 463:1, 203/[485]-212/[494]

To link to this article: http://dx.doi.org/10.1080/15421400601027932

Mol. Cryst. Liq. Cryst., Vol. 463, pp. 203/[485]–212/[494], 2007
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400601027932

Effect of Glass Transition Temperature on Compression and Elastic Properties of Poly(Meth)Acrylate Copolymer Thin Films and their Photoresist Patterns

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In order to study the effect of glass transition temperature (T_g) on the compression and elastic recovery properties of polymer, several poly(meth)acrylate copolymers having three or four segment units composed of methacrylic acid (MAA) and other vinyl monomers such as glycidyl methacrylate (GMA), styrene (STY), butyl acrylate (BAM), 2-hydroxyethyl methacrylate (HEMA), methyl methacrylate (MMA), benzyl methacrylate (BzMA), 2-ethylhexyl acrylate (EHA), octadecyl acrylate (ODA), ethyl acrylate (EAM), and lauryl methacrylate(LMA) were synthesized. The synthesized copolymers showed different glass transition temperatures depending on the component type. Thin films and micro patterns were prepared by photolithography process (spin coating/pre-baking/UV-exposure/KOH developing/post-baking) with prepared copolymer solution. The compression and recovery property of copolymer films and micro patterns were determined by nano indenter. As a result, copolymers with lower T_g especially MAA/GMA/STY, MAA/GMA/STY/BAM, and MAA/GMA/STY/HEMA copolymers showed higher compression and elastic recovery ratio.

Keywords: compression; glass transition temperature (T_g); micro patterns; poly (meth)acrylate; recovery ratio; thin films

The Korea Science and Engineering Foundation through the Hyperstructured Organic Materials Research Center supported this work. We acknowledge this support with thanks.

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1. INTRODUCTION

Photoresist polymers especially used in color filter have been required of improvement of the quality performance [1–6]. Along with the trend of enlarging the size of LCD panel, the column spacer has attracted a great deal of attention [7,8] because the movement of the spacer at high temperature and the generation of the bubbles at low temperature are prevented by using the plastic spacer with the thermal expansion coefficient close to that of liquid crystal. The column spacer provides improved contrast ratio, ripples free, uniformity, and surface hardness, etc. The thickness of the liquid crystal should be uniformly maintained by using the column spacer material with an appropriate compression recovery. The properties such as thermal stability [9], photosensitivity [10], roughness [11], glass transition temperature [12], and pattern resolution [13] of acrylic copolymers have been investigated for the negative and positive working photoresist. But the micro mechanical behavior in the form of thin film or patterns has not been studied sufficiently.

In order to study the effect of glass transition temperature on the compression property of poly(meth)acrylate copolymers, the authors designed and synthesized the poly(meth)acrylate copolymers having three or four segment units composed of methacrylic acid (MAA), glycidyl methacrylate (GMA), styrene (STY) and other (meth)acrylate (X). The compression property and thermal stability of prepared copolymers were investigated according to the variation of glass transition temperature (T_g) in the form of polymer thin film and micro patterns.

2. EXPERIMENTAL

Chemicals

The chemicals used in the preparation of poly(meth)acrylate copolymers were ACS grade. MAA, GMA, STY, BAM, HEMA, MMA, BzMA, 2-ethylhexyl acrylate (EHA), octadecyl acrylate (ODA), ethyl acrylate (EAM), and lauryl methacrylate (LMA) (Aldrich) were used without further purification. As the radical initiator, 2,2′-azobis(2,4-dimethylvaleronitrile) (ABDV) (WAKO) was used. Propylene glycol monomethyl ether acetate (PGMEA) (Aldrich) was used as the solvent. Dipentaerythritol hexaacrylate(DPHA) (Aldrich) was used as the photo-curable monomer. 1-2-octanedione-1[(4-phenylthio)phenyl]-2-o-benzoyl-oxime (ODPB) (Ciba-Geigy) and 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (BDMB) (Ciba-Geigy) were used as the photoinitiator. 0.04% (w/w) potassium hydroxide aqueous solution was used as the developer and distilled water for rinsing.

Synthesis of Poly(meth)acrylate Copolymers

Poly(meth)acrylate copolymers were synthesized as follows: MAA/GMA/STY copolymer was synthesized by the reaction of MAA, GMA, and STY (15/40/45 w/w composition in total monomer content) with ABDV for 8 h at 70°C under N_2 atmosphere in PGMEA. MAA/GMA/STY/X copolymer was prepared by the reaction of MAA, GMA, STY, and X monomer (15/20/45/20 w/w composition) with ADBV. BzMA/MAA copolymer was synthesized as the reference polymer by the reaction of BzMA and MAA (70/30 w/w) because it has been widely used in the negative photoresist.

Characterization

The structure of prepared copolymer was analyzed using FT-IR (Perkin-Elmer, Spectrum 2000) and ^{1}H-NMR (Varian, 500 NB) spectroscopy. FT-IR spectra were obtained from KBr pellets. The molecular weight (M_w) was measured by gel permeation chromatography (GPC) (WATERS 150 CV) with THF eluent. The decomposition temperature (T_d) was determined with a thermogravimetric analyzer (TGA) (Perkin Elmer TGA 7) in air atmosphere at a heating rate of 20°C/min. The glass transition temperature (T_g) was determined with differential scanning calorimeter (DSC) (Perkin Elmer DSC 7) in N_2 atmosphere at a heating rate of 10°C/min.

Preparation of Poly(meth)acrylate Copolymer Films and their Photoresist Patterns

The poly(meth)acrylate copolymer films (thickness, about 3.5 μm) were prepared by spin coating, pre-baking for 2 minutes at 100°C on hot plate, and post-baking for 30 minutes at 220°C in convection oven. In order to prepare copolymer micro patterns, the photoresist solutions were prepared in advance by mixing poly(meth)acrylate copolymer, DPHA, ODPB, and BDMB followed by filtration with a 0.45 μm membrane filter before coating. The photoresist patterns with the thickness of about 3.5 μm were prepared by spin-coating, pre-baking for 2 min at 100°C on hot plate, exposing to UV light with the intensity of 200 mJ/cm^2 (Thermo Oriel. UV EXPOSURE 6285, Proximity type), developing with 0.04% KOH aqueous solution, and finally post-baking for 30 minutes at 220°C.

Evaluation of the Compression and Elastic Properties of Copolymers

The thickness of films and patterns was measured with a surface profiler (Tencor Alpha-Step 200). The image of patterns was observed with scanning electron microscope (SEM) (Hitachi S-4300). The compression property of the prepared films and patterns was determined with the force of 5 gf, the loading speed of 0.45 gf/sec, and the holding time of 5 sec by nano indenter (Shimadzu Co. DUH-W201S-E) (Fig. 1). Triangular type indenter was used for thin film and planar type indenter for micro patterns. The compression recovery (%) was calculated according to the following expression:

$$\text{Compression recovery}\,(\%) = \frac{(D_1 - D_2)}{D_1} \times 100$$

where, D_1 is the indented depth at the force of 5 gf, D_2 is the depth indentation after removing force.

3. RESULTS AND DISCUSSION

The synthetic route for poly(meth)acrylate copolymer was shown in Scheme 1. By changing R_1 and R_2 substituents of X moiety in Scheme 1, designed poly(meth)acrylate copolymers having different glass transition temperatures (T_gs) were synthesized and characterized. The ^{1}H-NMR and FT-IR spectra of the MAA/GMA/STY/HEMA copolymer are presented in Figure 2 as a representative result. The signals of the HEMA methylene($-CH_2$) protons appeared at $\delta = 5.05$ ppm, aromatic STY protons at $\delta = 6.5$–7.5 ppm in Figure 2-(a). The hydroxyl protons signal of the HEMA and MAA was observed at 11.9 ppm. The signals of OH and carbonyl bands in Figure 2-(b) are

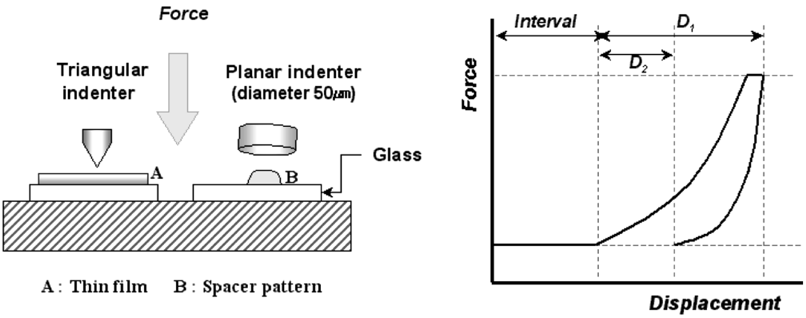
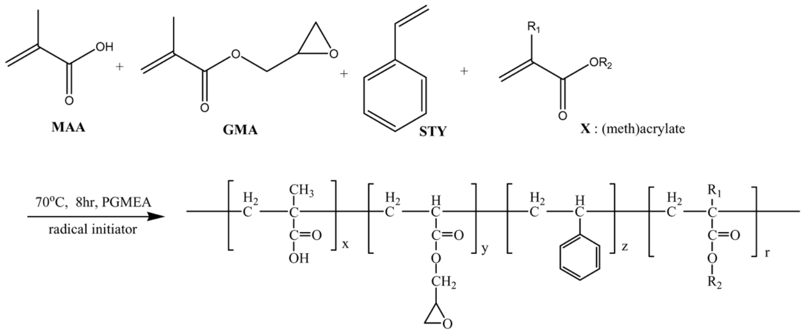
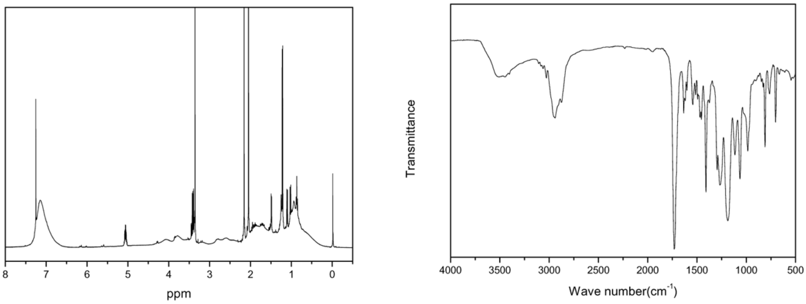


FIGURE 1 The nano-indenter and compression graph.



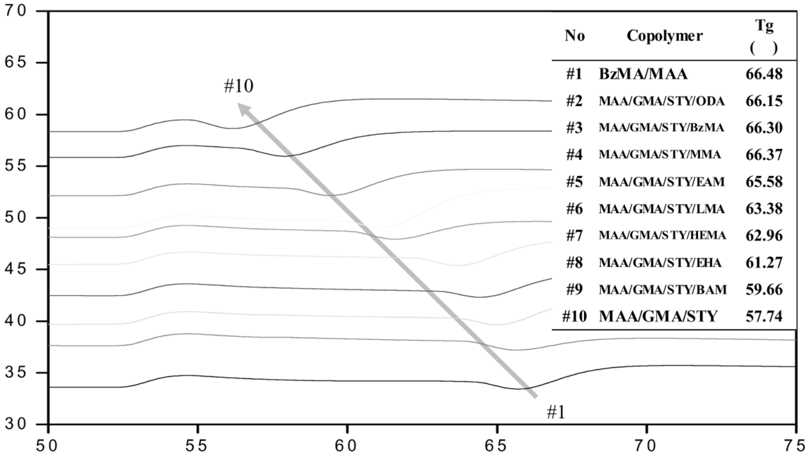
SCHEME 1 The synthetic route for poly(meth)acrylate copolymer.

presented at 3200–3400 and 1720 cm^{-1}, respectively. The configuration data of other copolymers are not listed in this paper. Figure 3 shows DSC spectra of copolymers. All T_gs of copolymers were obtained at the range of 55–70°C and assumed to be influenced by the X monomer unit introduced in the copolymer chain. TGA curves for the prepared polymers are shown in Figure 4. All of the prepared copolymers have good thermal stability by showing high T_d of over 300°C being suitable for the photoresist use. The chemical composition, T_g, and T_d data of copolymers are summarized in Table 1. As shown in Table 1, the copolymers of MAA/GMA/STY, MAA/GMA/STY/X, and BzMA/MAA showed different T_gs. MAA/GMA/STY, MAA/GMA/STY/BAM, MAA/GMA/STY/EHA, MAA/GMA/STY/HEMA, and MAA/GMA/STY/LMA showed lower T_gs and higher T_ds. MAA/GMA/STY, MAA/GMA/STY/BAM, and MAA/GMA/STY/HEMA copolymers showed good compression indentation and recovery ratio in the form of film and pattern. Table 2



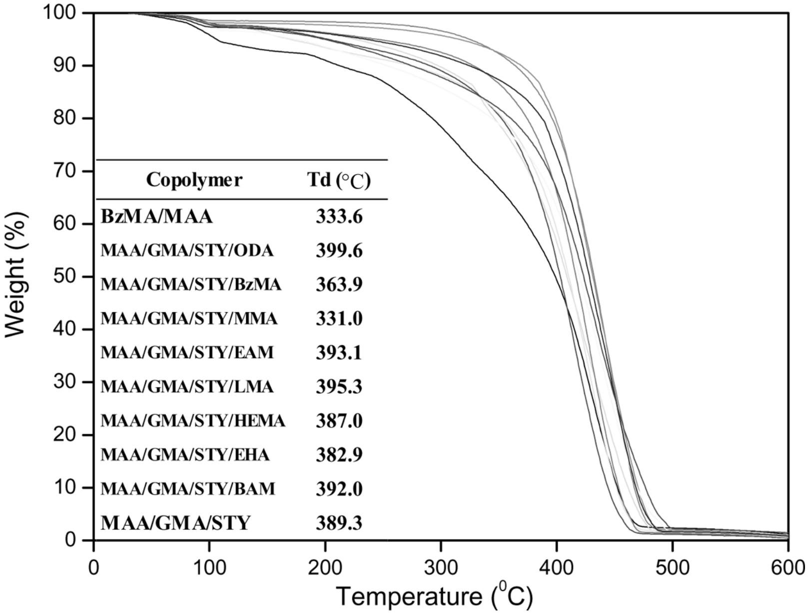
(a) (b)

FIGURE 2 ^{1}H-NMR and FT-IR spectra of prepared MAA/GMA/STY/HEMA copolymer.



No	Copolymer	Tg ( )
#1	BzMA/MAA	66.48
#2	MAA/GMA/STY/ODA	66.15
#3	MAA/GMA/STY/BzMA	66.30
#4	MAA/GMA/STY/MMA	66.37
#5	MAA/GMA/STY/EAM	65.58
#6	MAA/GMA/STY/LMA	63.38
#7	MAA/GMA/STY/HEMA	62.96
#8	MAA/GMA/STY/EHA	61.27
#9	MAA/GMA/STY/BAM	59.66
#10	MAA/GMA/STY	57.74

FIGURE 3 DSC curves of various poly(meth)acrylate copolymers.



Copolymer	Td (°C)
BzMA/MAA	333.6
MAA/GMA/STY/ODA	399.6
MAA/GMA/STY/BzMA	363.9
MAA/GMA/STY/MMA	331.0
MAA/GMA/STY/EAM	393.1
MAA/GMA/STY/LMA	395.3
MAA/GMA/STY/HEMA	387.0
MAA/GMA/STY/EHA	382.9
MAA/GMA/STY/BAM	392.0
MAA/GMA/STY	389.3

FIGURE 4 Thermogravimetric analysis of various poly(meth)acrylate copolymers.

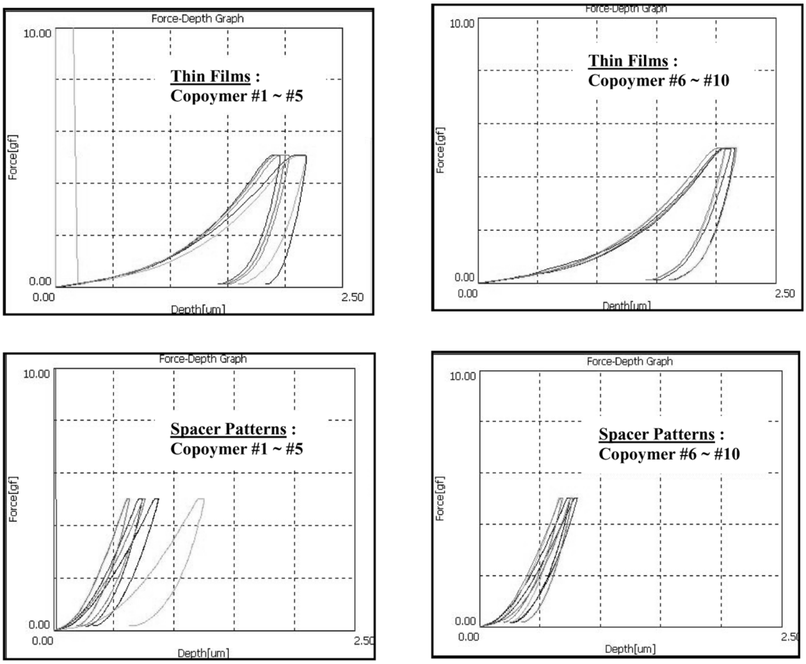
TABLE 1 The Composition and Properties of Prepared Poly(meth)acrylate Copolymers

No.	R1*	R2*	Copolymer	Composition (wt/wt%)	Mw	T_g(°C)	T_d(°C)
#1	–	–	BzMA/MAA	83/17	14,4000	66.48	333.6
#2	CH_3	octadecyl	MAA/GMA/STY/ODA	15/20/45/20	8,750	66.15	399.6
#3	CH_3	benzyl	MAA/GMA/STY/BzMA	15/20/45/20	9,780	66.30	363.9
#4	CH_3	methyl	MAA/GMA/STY/MMA	15/20/45/20	8,450	66.37	331.0
#5	H	ethyl	MAA/GMA/STY/EAM	15/20/45/20	7,432	65.58	393.1
#6	CH_3	lauryl	MAA/GMA/STY/LMA	15/20/45/20	7,210	63.38	395.3
#7	CH_3	2-hydroxyethyl	MAA/GMA/STY/HEMA	15/20/45/20	11,588	62.96	387.0
#8	H	2-ethylhexyl	MAA/GMA/STY/EHA	15/20/45/20	12,790	61.27	382.9
#9	H	butyl	MAA/GMA/STY/BAM	15/20/45/20	7,530	59.66	392.0
#10	–	–	MAA/GMA/STY	15/40/45	7,288	57.74	389.3

*R1 and R2 are the substituents of X monomer in Scheme 1.

TABLE 2 The Compression and Elastic Properties of Various Poly(meth)acrylate Copolymers

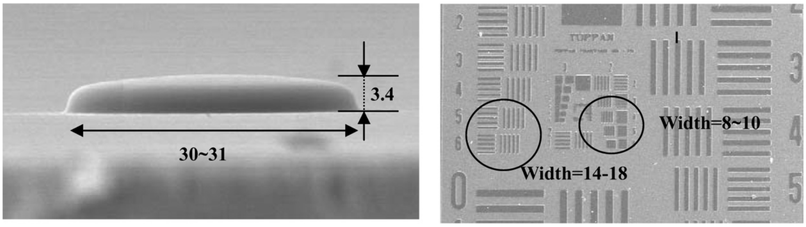
		Thin-Films					Column Spacer Patterns					
			Deformation						Deformation			
No.	Prepared Coploymer	Thickness (T, μm)	TOTAL D1 (μm)	PLASTIC D2 (μm)	ELASTIC D1-D2 (μm)	Recovery Ratio (%)	Thickness (T, μm)	Pattern Width (μm)	TOTAL D1 (μm)	PLASTIC D2 (μm)	ELASTIC D1-D2 (μm)	Recovery Ratio (%)
#1	BzMA/MAA	3.166	2.191	1.83	0.361	16.5	3.386	33.33	0.871	0.324	0.547	62.8
#2	MAA/GMA/STY/ODA	3.223	2.188	1.586	0.602	27.5	3.370	27.38	1.251	0.621	0.630	50.4
#3	MAA/GMA/STY/BzMA	3.145	2.042	1.486	0.556	27.2	3.462	37.59	0.759	0.230	0.529	69.7
#4	MAA/GMA/STY/MMA	3.305	2.006	1.445	0.561	28.0	3.352	34.92	0.628	0.182	0.446	71.0
#5	MAA/GMA/STY/EAM	3.096	1.964	1.41	0.554	28.2	3.673	31.75	0.736	0.261	0.475	64.5
#6	MAA/GMA/STY/LMA	3.153	2.172	1.606	0.566	26.1	3.117	30.95	0.878	0.37	0.508	57.9
#7	MAA/GMA/STY/HEMA	3.156	2.078	1.406	0.672	32.3	3.339	39.68	0.678	0.245	0.433	63.9
#8	MAA/GMA/STY/EHA	3.343	2.158	1.599	0.559	25.9	3.563	32.14	0.751	0.262	0.489	65.1
#9	MAA/GMA/STY/BAM	3.675	2.128	1.466	0.662	31.1	3.516	36.90	0.807	0.261	0.546	67.7
#10	MAA/GMA/STY	3.542	2.073	1.406	0.667	32.2	3.422	37.52	0.69	0.193	0.497	72.0



(a) (b)

FIGURE 5 The compression and elastic behavior graph of (a) copolymers thin films and (b) micro patterns of poly(meth)acrylate photoresist in the process of introducing and removing the compression 5gf.

and Figure 5 show the nano indentation results of the polymer thin films and micro patterns. MAA/GMA/STY copolymer showed highest elastic property (recovery ratio) in both of film (32.2%) and pattern (72%). Copolymers such as MAA/GMA/STY/LMA and MAA/GMA/STY/EHA



(a) (b)

FIGURE 6 The SEM and optical microscope image of (a) the column spacer pattern and (b) line patterns.

showed low T_g but presented relatively low recovery ratio. It might be due to the softness originated from the longer side chine length. Figure 6 shows SEM and optical microscope image of photoresist patterns prepared with MAA/GMA/STY copolymer as a representative result. Figure 6-(a) shows typical column spacer pattern with the thickness of 3.4 µm and the width of 30 µm obtained for compression test. It is suggested that this pattern can be used as column spacer for industrial purpose. Figure 6-(b) shows the resolution of line pattern which illustrates the size 10 µm under.

4. CONCLUSION

For the purpose of investigating the effect of T_gs on the polymer films and column spacer patterns, several poly(meth)acrylate copolymers were designed, synthesized, and characterized. All of the prepared copolymers showed good thermal stability. Copolymers of MAA/GMA/STY, MAA/GMA/BAM, and MAA/GMA/STY/HEMA showed lower T_g and better elastic behavior in the form of thin film and micro pattern compared to that of BzMA/MAA copolymer being used widely for negative photoresist.

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