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Synthesis of Novel Ester Acetal Polymers for Computer-to-Plate Applications

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Abstract. *Novel ester acetal polymers were synthesized by the polymerization reaction of aromatic dicarboxylic acids with 1,4-cyclohexanedimethanol divinyl ether in organic solvent under heating. The obtained polymers show good solubilities in common organic solvents and high thermal stability. The number-average molecular weights of the ester acetal polymers range from 5000 to 7000 with M_w/M_n of 2.0–3.0. The polymers can undergo acidolytic reaction rapidly at room temperature or at a slightly higher temperature. By making use of the high acidolytic activity of the ester acetal polymers, new imaging materials can be developed for thermal sensitive plates in computer-to-plate (CTP) and UV-CTP applications.*

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INTRODUCTION

In recent years, digital printing has been developed rapidly due to a growing demand for high quality and fast reproduction. In particular, computer-to-plate (CTP) technology, which can achieve the process of transferring digital files from computer directly to printing plates, is now the focus of digital printing due to its various advantages such as better quality, higher production efficiency, less pollution than conventional printing techniques, and so on.[1,2] Thermal sensitive CTP, which uses an infrared laser as the radiation source, and UV-CTP, which uses a near UV laser as the radiation source, are two of the main CTP technologies. CTP plates are the key to the widespread employment of CTP technology. Therefore, much attention has been paid to find new imaging materials for CTP plates that exhibit excellent performance such as high photosensitivity.[3–8]

Chemical amplification (CA) has been widely applied on photoresists to enhance the photosensitivity. For the positive-tone CA resist system, which mostly consists of binder resin, dissolution inhibitor and photoacid generator (PAG), a large difference of dissolution rate between the imaging area and the non-imaging area is realized by an acid-catalyzed deprotection reaction of a polymer containing an acid-labile group.[9] Chemically amplified positive-tone UV photoresists display higher photosensitivity than conventional diazonaphthoquinone (DNQ)–phenolic-resin systems and can be used for UV-CTP plates. When infrared dye is added into CA photoresists then imaging material for thermal sensitive CTP plates is formed. Under infrared radiation, the infrared dye can convert the energy of the infrared light into heat, which makes the PAG decompose to generate strong acid.[10–12] It is apparent that the dissolution inhibitors and their acidolytic activity are key factors for the performance of the imaging materials.

It has been reported that the ester acetal group can be eliminated under mild acidic conditions.[13–15] Thus, polymers which contain ester acetal structure in the main chain can be cleaved under acid catalysis to give lower molecular weight segments and are expected to be applied for chemically amplified imaging materials.[16,17] In this study, novel ester acetal polymers were synthesized from aromatic dicarboxylic acids and 1,4-cyclohexanedimethanol divinyl ether. The preparation process of the polymers is shown in Scheme. The characterization and acidolytic activity of the ester acetal polymers were investigated, and the properties of the imaging materials containing the polymers were also studied for CTP plates.

EXPERIMENTAL

Materials

1,4-Cyclohexanedimethanol divinyl ether (CHDDE) was purchased from Aldrich China. Propylene glycol monomethyl ether acetate (PGMEA) was obtained from Aladdin Reagents Company (Shanghai, China). 1,4-Naphthalenedicarboxylic acid (1,4-NDA), terephthalic acid (TPA), isophthalic acid (IPA) and other organic solvents were obtained from Beijing Chemical Reagents Company (Beijing, China). All the reagents were used as received. The triazine PAG, 2-(2-naphthalen-1-vinyl)-4,6-bis-trichloromethyl-[1,3,5]triazine, is an industrial product, which was used without further purification.

Measurements

^{1}H nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance III 400 MHz spectrometer using tetramethylsilane (TMS) as an internal standard in chloroform-*d* ($CDCl_3$) or acetone-d_6. FTIR spectra were obtained with a Nicolet Avatar 360 spectrometer. Thermogravimetric analysis (TGA) was performed on a ZRY-2p simultaneous thermal analyzer (Shanghai Precision & Scientific instrument Co., Ltd.) at a heating rate of 10°C min^{-1} under a nitrogen flow of 20 mL min^{-1}. The glass transition temperature (T_g) of the polymers

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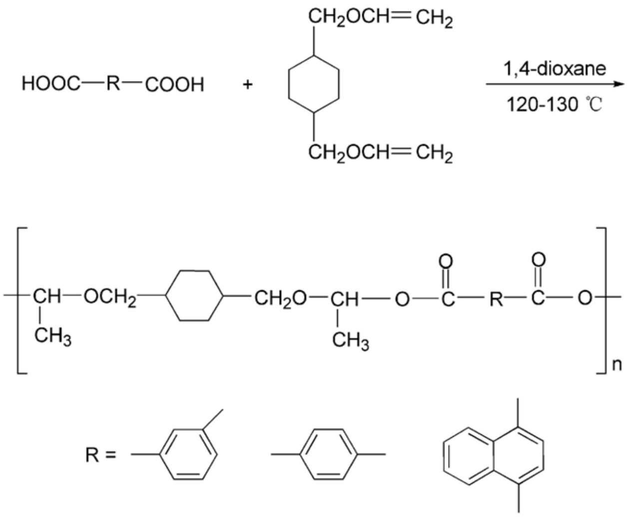

Scheme 1. Preparation of the ester acetal polymers.

was determined by using differential scanning calorimeter (DSC) measurement performed on a Mettler DSC 30 system instrument at a heating rate of 10°C min^{-1} under nitrogen. The number-average (M_n) and weight-average (M_w) molecular weights of the polymers were measured using a Polymer Laboratories gel permeation chromatograph (PL GPC50) equipped with PLgel mixed-C, with tetrahydrofuran as solvent at 40°C with a 1.0 mL min^{-1} flow rate. Polystyrene (PS) standards were used for calibration. A medium pressure Hg lamp (365 nm) was used as an exposure tool to study the acidolysis property. Photolithographic experiments were carried out on an i-line exposure system (Nikon Corporation, model NSR2005I9C). SEM micrographs were obtained with a KLA-Tencor 8250 CD-SEM system.

Polymer synthesis

A typical example of polymerization of aromatic dicarboxylic acid with CHDDE is described as follows. TPA (5.0 g, 30 mmol), CHDDE (5.9 g, 30 mmol) and 1,4-dioxane (10 mL) were added into a three-necked flask equipped with a magnetic stirrer, a nitrogen inlet and a condenser. The mixture was stirred at 120–130°C under nitrogen for 3–5 h. After the completion of the reaction, the mixture was poured into a large amount of petroleum ether to give a precipitate, which was then dried in vacuum to yield the ester acetal polymer poly(TPA–CHDDE). Yield: 80%. IR (KBr, cm^{-1}): 2919, 2856 ($-\mathrm{CH}_3$ and $-\mathrm{CH}_2$), 1717 ($-\mathrm{C}=\mathrm{O}$ of $-\mathrm{COOR}$). ^{1}H NMR (400 MHz, CDCl_3): δ (ppm) 8.1 (s, phenyl protons), 6.1 (s, methenyl protons), 3.5 ($-\mathrm{CH}_2\mathrm{O}-$), 2.0–0.9 (alicyclic and aliphatic protons).

Lithographic experiments

The photosensitive composition was formulated by dissolving poly(1,4-NDA–CHDDE), phenolic resin and triazine PAG with a mass ratio of 1:3:0.06 in PGMEA. The solution was filtered with a 0.2 μm Teflon membrane filter and then spin-coated onto silicon wafers pre-treated with HMDS and pre-baked at 100°C for 60 s to remove the solvent. A resist film about 1 μm thick was formed. Exposure was carried out in a Nikon NSR2005I9C stepper. The exposed films were developed in a 2.38 wt% tetramethylammonium hydroxide (TMAH) aqueous solution for 60 s.

Infrared dye was added into the above photosensitive composition in the same amount as triazine to form positive-tone imaging material for thermal sensitive CTP plates. The thermal sensitive composition was spin-coated onto an aluminum substrate and then baked at 100°C for 60 s to remove the solvent. The thermal sensitive plate was scanned with an 830 nm laser and developed in a dilute aqueous base (5 wt% sodium silicate).

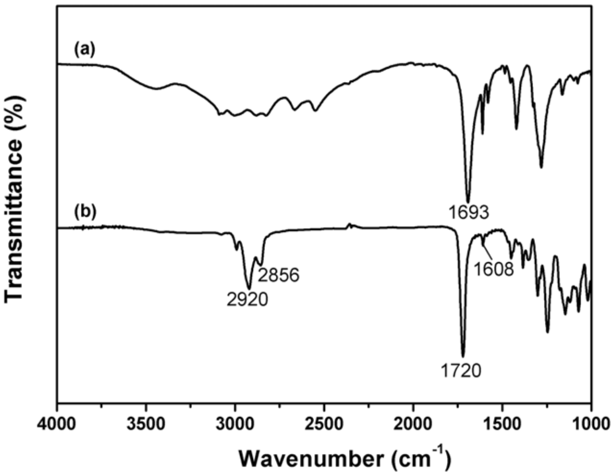

Figure 1. FTIR spectra of (a) IPA and (b) poly(IPA–CHDDE).

RESULTS AND DISCUSSION

Polymer synthesis

It has been reported that dicarboxylic acids can react with divinyl ether compounds to give the corresponding ester acetal polymers in the presence of an acidic catalyst.[18] In our work, the ester acetal polymers were prepared by the polymerization reaction of the aromatic dicarboxylic acids with CHDDE under heating without catalyst. The polymerization reaction can be investigated by the FTIR spectra of the reaction mixture. Taking the reaction of IPA and CHDDE as an example, as the reaction proceeded, the absorption peak of the carboxylic acid at 1693 cm^{-1} gradually reduced and a new absorption peak at 1720 cm^{-1} appeared and gradually strengthened, indicating the presence of a carbonyl group of ester. Meanwhile, the absorption peaks of the vinyl group at 1614 cm^{-1} and 1634 cm^{-1} weakened and finally disappeared at the end of the reaction. The FTIR spectra of IPA and the polymerization reaction product poly(IPA–CHDDE) are shown in Figure 1. Furthermore, the structure of poly(IPA–CHDDE) was also confirmed by its ^{1}H NMR spectrum. In the ^{1}H NMR spectrum of the polymer, a sharp single peak around δ 6.1 ppm can be assigned to methenyl protons of the ester acetal groups formed in the polymerization reaction (Figure 2). These results clearly demonstrate that the polymerization reaction between IPA and CHDDE had been completed to give the poly(IPA–CHDDE).

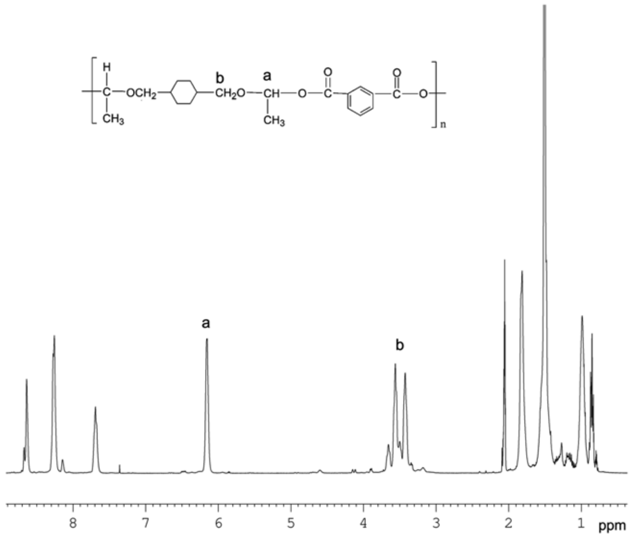

Figure 2. ^{1}H NMR spectrum of poly(IPA–CHDDE) in acetone-d_6.

1,4-Dioxane is found to be the optimal solvent for the polymerization reactions. Solvents with lower polarity, such as xylene and cyclohexanone, cannot be used because of the insolubility of the aromatic dicarboxylic acids, whereas proton type solvents, such as ethylene glycol monoethyl ether, will result in an incomplete reaction or even the production of a by-product. Among the three aromatic dicarboxylic acids, the polymerization reaction rate of TPA is much lower than that of 1,4-NDA and IPA. The polymerization reaction of 1,4-NDA and CHDDE can be completed within 3–5 h at 120–130°C. The reaction of IPA and CHDDE was conducted in the same way and for the same reaction time to give the polymerized product poly(IPA–CHDDE), but the reaction of TPA and CHDDE needs a longer reaction time of 18–24 h to finish. This is probably because of the lower solubility of TPA in the reaction solvent. Generally, the polymerization reaction can occur even below 100°C, but a higher reaction temperature is beneficial to enhance the reaction rate. However, the reaction will become complicated if the reaction temperature is raised to over 140°C because the FTIR spectrum of the reaction mixture indicated an incomplete reaction even with a much longer time than ordinarily needed.

Polymer characterization

The ester acetal polymers can be dissolved easily in common solvents such as acetone, 1,4-dioxane, xylene, chloroform, tetrahydrofuran (THF), PGMEA, ethyl lactate and ethylene glycol monoethyl ether, but not dissolved in methanol or ethanol.

The molecular weights of the ester acetal polymers were measured by GPC and are listed in Table I. The measured number-average molecular weights generally range from 5000 to 7000 with M_w/M_n of 2.0–3.0. The molecular weights of the polymers are not very high but are suitable for imaging materials.

Table I. Characterization data of the ester acetal polymers.

Entry	Polymer	M_n ($\times 10^4$)	M_w ($\times 10^4$)	M_w/M_n	T_g (°C)	T_d (°C)
1	TPA–CHDDE	0.65	1.4	2.1	61	226
2	IPA–CHDDE	0.62	1.9	3.0	30	226
3	1,4-NDA–CHDDE	0.63	1.4	2.2	60	230

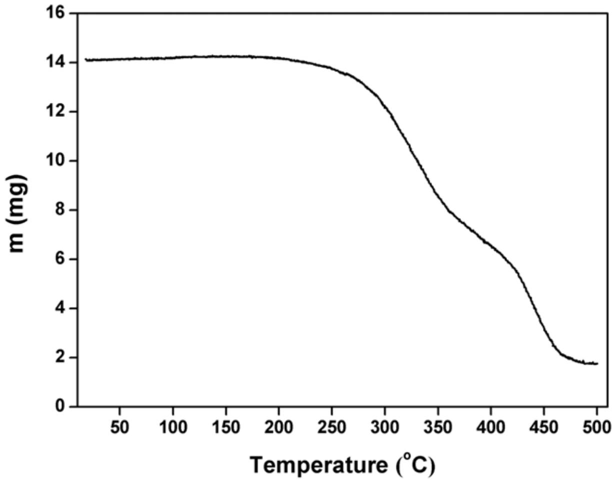

Figure 3. TGA curve of poly(1,4-NDA–CHDDE).

The thermal stability of the ester acetal polymers was investigated by TGA. The TGA traces of the polymers, all of which showed similar TGA curves, as seen in Figure 3 using poly(1,4-NDA–CHDDE) as an example, displayed that up to 200°C there was little significant change, and then at about 230°C thermal decomposition occurred. Therefore, this decomposition temperature clearly demonstrates the high thermal stability of the ester acetal polymers. The initial decomposition temperatures (T_d) of the polymers are presented in Table I. In addition, the T_g values of the polymers were measured by DSC and are also shown in Table I. The comparatively low T_g values of the polymers are because of the flexible chain of the ester acetal polymers. Among these polymers, the T_g of poly(IPA–CHDDE) is the lowest.

Acidolysis activity

The ester acetal linkage of the polymers can be cleaved by strong acid generated by PAG. To investigate the acidolysis activity of the polymers, a film of poly(IPA–CHDDE) containing 3 wt% triazine PAG was exposed to a UV lamp with an exposure dose of about 60 mJ cm^{-2}. Figure 4 shows the FTIR spectra of the film cast on a NaCl plate before and after exposure to UV light. It can be seen that the FTIR spectrum of the film displays no apparent change after exposure without post-exposure bake, indicating no acidolysis reaction at room temperature. After being exposed and baked at 80°C for 120 s, the absorption peak of the ester group at 1720 cm^{-1} was transformed to that of carboxylic acid at 1693 cm^{-1}, indicating that the acidolysis reaction at a low PEB temperature is very rapid and can result in a high dissolution rate of the exposed distract. Additionally, it

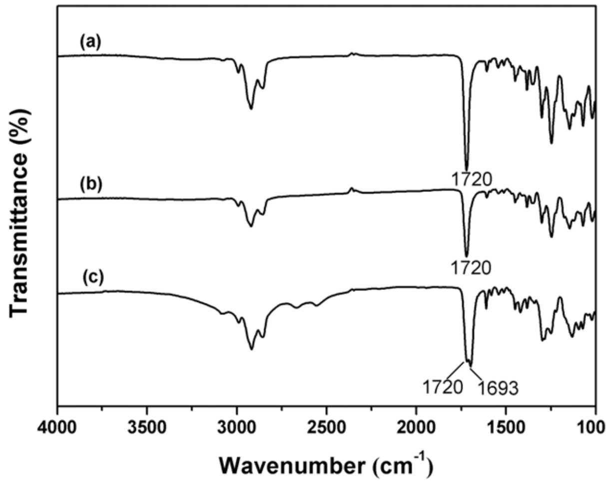

Figure 4. FTIR spectra of poly(IPA–CHDDE) film containing 3 wt% triazine PAG. (a) Before exposure, (b) after exposure (dose = 60 mJ cm^{-2}) without post-exposure bake and (c) after exposure and baking at 80°C for 120 s.

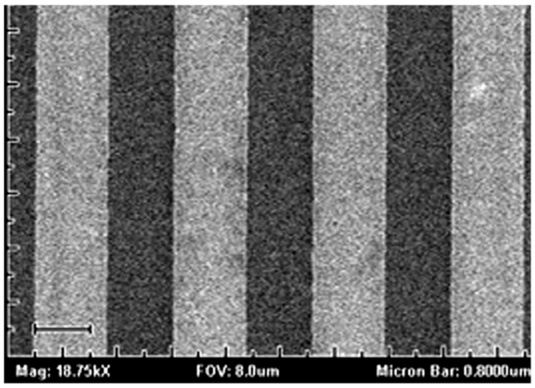

Figure 5. SEM image of positive-tone pattern with a resolution of 1 μm.

was found that the acidolysis activity of poly(TPA–CHDDE) is similar to that of poly(IPA–CHDDE), which needs a low PEB temperature to complete the acidolysis reaction, whereas the acidolysis reaction of poly(1,4-NDA–CHDDE) can occur rapidly at room temperature under the same experiment conditions. These experimental results indicate that chemically amplified photolithographic materials can be formed by the polymers and photoacid generators.

Lithographic evaluation

The chemically amplified photolithographic material formulated with phenolic resin, poly(1,4-NDA–CHDDE) and triazine PAG was evaluated using an i-line stepper. As shown in Figure 5, a clear positive-tone pattern was obtained with a resolution of 1 μm at an exposure dose of 45 mJ cm^{-2}. The photosensitivity of the new imaging material is higher than that of the common DNQ–phenolic-resin system which is generally larger than 60 mJ cm^{-2} and suitable for UV-CTP. Among these polymers, poly(1,4-NDA–CHDDE) is preferred because its acidolytic reaction can proceed at room temperature.

Infrared dye was added into the above photosensitive composition to form thermal sensitive imaging material. The performance of the thermal sensitive composition was evaluated using an infrared laser exposure instrument. The photosensitivity was about 95 mJ cm^{-2} and the mesh point reduction could achieve 1%–99%. In addition, the thermal sensitive CTP plates showed high film remaining rate ($\geq$95%) and good development latitude.

CONCLUSION

Novel ester acetal polymers can be synthesized by the polymerization reaction of aromatic dicarboxylic acids with 1,4-cyclohexanedimethanol divinyl ether under heating without catalyst. These polymers exhibit good solubilities in common organic solvents and high thermal stability. The polymers can undergo acidolytic reaction rapidly at room temperature or at a slightly higher temperature because of the cleavage of the ester acetal linkage of the polymer chain catalyzed by strong acid. New positive-tone photolithographic materials can be formulated with the ester acetal polymers, phenolic resin and triazine PAG and display good resolution and high photosensitivity in lithographic experiments using an i-line stepper. The new imaging materials are good choices for UV-CTP plates due to their high photosensitivity. By adding infrared dye into the above photosensitive composition, imaging materials for positive-tone thermal sensitive CTP plates were formed, which show excellent performance in photosensitivity, mesh point reducibility, film remaining rate and development latitude in CTP experiments. Therefore, ester acetal polymers are key components in forming new imaging materials for CTP plates.

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