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Synthesis and Characterization of Methacrylate-based Copolymers for Integrated Optical Applications

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Poly(methylmethacrylate/2-methacryloylethylmethacrylate)-based copolymers of varying composition have been synthesized and characterized. Free-radical polymerization of hydroxyethylmethacrylate and methylmethacrylate over a range of monomer feed ratios gives an ideal random copolymer series which has been functionalized by further methacryloylation of the pendant hydroxyl group. The resulting polymers have been cross-linked both thermally and by UV exposure, as evidenced by infrared and solid state NMR spectroscopy. After thermal crosslinking the polymers remain stable up to 200°C. Variation of polymer composition has allowed the refractive index to be tuned between 1.497 and 1.518, a range suitable for waveguide applications, and channel waveguides have been fabricated by UV writing. The propagation loss of these channel waveguides is less than 1dB/cm at a range of near IR wavelengths.

Introduction

Organic polymers have found many applications in electronic and optical devices[1-3]. They offer process compatibility, flexibility in design, and the ability for integration of electronic and optoelectronic functions. Whilst inorganic optical materials such as glass and silica show excellent performance in optical devices, such materials are usually difficult to process and, as a result, devices made from these are expensive. Thus, the use of organic polymers for optical telecommunication applications has become increasingly attractive because of their cost- effective technology.

Numerous polymer systems have been developed for optical applications[4-15], the key requirement imposed for such materials being transparency. Much interest has focussed on acrylic polymers because of their well-known optical properties and good film-forming capability[16-18]. Although acrylic polymers, especially polymethylmethacrylate (PMMA), are common materials for optical polymers, little interest has as yet been shown in the use of a self-crosslinkable PMMA polymer for this purpose. Whilst three-, four- and five-component polymer systems incorporating several functional esters attached to a methacrylate-based core have previously been described for use in lithographic systems[19] the application of co-polymers of the type reported here for wave-guide applications is novel. The present work explores the use of a series of compositions of an acrylate-based self-crosslinkable copolymer poly(methylmethacrylate/2-methacryloylethylmethacrylate) poly(MMA/MAOEMA) (scheme 1) in waveguides. Polymers described in the present work are self-crosslinkable both thermally and by UV exposure. A further requirement of such polymers is the ability to control their refractive index[20]. We have prepared copolymers of methylmethacrylate (MMA) and hydroxyethylmethacrylate (HEMA) the latter component being used to provide pendant hydroxyl groups capable of further functionalization (by reaction with methacrylic anhydride - see scheme 1). These copolymers have a suitable refractive index range (refractive index of poly(HEMA) = 1.520[20]) for use in waveguide systems.

<Scheme 1>

Conventionally polymer channel waveguides are fabricated using photolithographic techniques. However direct UV-witing[21] has recently been explored since it greatly simplifies complex device fabrication. In the present study we have used UV writing techniques to create channel waveguides. We describe here the preparation of a copolymer of MMA and

HEMA and its conversion to P(MMA/MAOEMA). We discuss the characterization, UV absorptivity, thermal properties, evidence for crosslinking, and refractive index of the resulting materials. Finally we describe the creation of a waveguide using such polymers.

Experimental Section

Materials and Instruments

A series of MMA/HEMA copolymers were obtained by radical copolymerization of monomers (MMA, HEMA) in the presence of azoisobutyronitrile (AIBN). MMA, HEMA, methacryloyl chloride (MACl), and methacrylic anhydride (MAAN) were purchased from Aldrich and were purified by distillation. Triethylamine (Et_3N), dimethyl formamide (DMF), and dichloromethane (DCM) were distilled prior to use. AIBN obtained from Acros was purified by recrystallization from methanol (MeOH). *p*-Benzoquinone (*p*-BzQ) was recrystallized from 1:1 mixture of water and ethanol. Methyl ethyl ketone (MEK), MeOH, ethanol (EtOH) and 1-methoxy-2-propanol acetate (propylene glycol methyl ether acetate – PGMEA) were purchased as spectroscopic grade materials and used without further purification.

^1H NMR spectra were recorded on a Bruker AC 300 MHz using $CDCl_3$ or d_6-DMSO as solvent. ^{13}C-CPMAS solid-state NMR spectra were recorded at 75MHz using a Varian UNITY*Inova* spectrometer[22] FT-IR spectra were recorded on a Perkin-Elmer 2000 FT-IR instrument. UV-Visible absorption spectra were measured with a Perkin-Elmer Lambda 9 UV/Visible/Near IR spectrophotometer. GPC (gel permeation chromatography) was carried out using Waters 150CV equipment and calibrated with polymethylmethacrylate. Polymer films were prepared using a spin-coater from Headway Research. Film thickness was measured by α-step of Tencor Instrument, Jobin Yvon ellipsometry, and prism coupler. Thermal properties were measured using a Perkin-Elmer DSC 7 differential scanning calorimeter and a Polymer Laboratories PL7 STA 1500H TGA thermal gravimetric analyser. Polymer films were processed by exposure to a low pressure mercury UV UVP pen-ray lamp. Refractive indices were measured by ellipsometry or by prism coupling as appropriate. The channel waveguides were written using a cw (continuous wave) frequency-doubled argon-ion laser (244nm). The mode profile of channel waveguides was taken using a laser beam analyzer LBA-100A.

*Preparation of copolymers **4a** containing ca. 47% HEMA*

A mixture of MMA (10.62 g, 100 mmol) and HEMA (12.16 g, 90 mmol) was dissolved in MeOH (62 ml) under a slow stream of nitrogen at 60 °C for 30 minutes prior to the addition of AIBN (0.66 g, 3.8mmol). The reaction mixture was then stirred at reflux under nitrogen for 23 h, after which it was cooled and diluted by pouring with stirring into ether (1L). A white powder formed which was dried *in vacuo*, redissolved in methanol (100 ml), reprecipitated into ether (1 L) and dried to give purified polymer (**4a**) (17.70g, 78%).

^{1}H NMR (300 MHz, DMSO) δ 3.60 (s, br, $-OCH_3$), 3.65 and 3.90 (s, br, $-CH_2CH_2-$). FT-IR (NaCl) ν (cm^{-1}) 1700 (C=O), 3500 (-OH).

*Preparation of polymer **11e** by methacryloylation of **4b** using methacrylic anhydride (MAAN)*

Poly(MMA/HEMA) (53:47) (2.85 g, 25 mmol), in dry DCM (25 ml) was stirred under nitrogen prior to the addition of E_3N (8 ml, 59 mmol). After 10 min, MAAN (9 ml, 59 mmol) was added drop-wise. The reaction mixture was stirred under nitrogen for a further 4 h. The polymer was isolated by precipitation in ether (200mL). The resulting glassy solid was isolated, dissolved in DCM (20 ml) and reprecipitated in ether (200 ml). The glassy solid was finally redissolved in DCM (20 ml), reprecipitated by pouring to n-hexane (1 L), and dried to give methacryloylated polymer (**11e**) (3.07g, 83 %).

^{1}H NMR (300 MHz, $CDCl_3$) δ 3.60 (3H, s, $-CH_3$), 4.20 (2H, br s, $-\underline{CH_2}CH_2-$), 4.35 (2H, br s, $-CH_2\underline{CH_2}-$), 5.65 (1H, br, $CH_2=C$), 6.15 (1H, br, $CH_2=C$). FT-IR (NaCl) ν (cm^{-1}) 1700 (C=O), 1637 (C=C).

Polymer film preparation

Solutions of either (a) HEMA-rich copolymers dissolved in DMF, (b) MMA-rich copolymers dissolved in MEK, or (c) methacryloylated polymers dissolved in either PGMEA or a cosolvent of PGMEA and MEK (3:1 by weight percent), were filtered through a 0.2 μm PTFE membrane filter and spin-coated (at 1,000 ~ 4,000 rpm) onto silicon or silica substrates, the film thickness being controlled by adjustment of the solution concentration from 10 to 40 wt%. The spin-coated films were then dried at 90°C for 5 min to remove residual solvent.

Results and Discussion

*Preparation of Copolymers of MMA and HEMA **(1-6)***

The procedure for copolymerization is outlined in Scheme 1. Different polymer compositions were prepared by thermally initiated free-radical polymerization of MMA and HEMA using varying monomer ratios (0, 10, 20, 34, 47, 70, 85, and 100%-HEMA-content copolymers) in either MEK (for all preparations including MMA-rich copolymers) or alcohol (for >34% HEMA-content copolymers). Solution polymerization required that both monomer and the resulting polymer should be soluble under the reaction conditions in order to avoid precipitation which would result in a decreased degree of polymerization and reaction rate. Methanol was the preferred reaction solvent for the preparation of HEMA-rich copolymers which showed poor solubility in MEK. The resulting copolymers were precipitated into ether. Changing the reaction time (typically 24h at 60°C) for polymerization was found to have little effect on the degree of conversion. In order to explore whether a change in the amount of initiator, or the ratio of monomer weight to volume of solvent would have a significant effect on the molecular weight of the polymer, we prepared several batches of polymer using different initial conditions (see Table 2, entries **2a**, **2b** and **2c**). Little variation in the molecular weight distribution was observed.[#] The molecular weight (M_w) of **4b** prepared using 2mol% AIBN and a 0.34 ratio of monomer weight to volume of solvent used was determined to be ca. 138,000 by GPC (gel permeation chromatography). A previous report[23] suggests that this value lies in the region where PMMA polymers give best film-forming performance. GPC studies of our polymer samples revealed that these have molecular weight polydispersity in the range 1.7 to 2.9 (values which are typical for batch free radical polymerization). The results of the copolymerization reactions are summarized in Table 1.

<Table 1>

In general, composition of copolymer was well matched to the ratios of monomers used as determined by ^{1}H NMR spectroscopy (see Table 1). Repeated preparations using the same monomer feed ratio gave reproducible results. The data in Table 1 suggest that the materials described here are ideal copolymers with excellent composition reproducibility.

*Methacryloylation of Copolymer **(8-13)***

The procedure for methacryloylation of the P(MMA/HEMA) is outlined in Scheme 1. The most important requirements of this process are (i) to achieve the highest possible degree of methacryloylation of the pendant hydroxyl groups, and (ii) to avoid polymer cross-linking during the reaction. The hydroxyl bond has strong absorptions in the near IR region at 1.3 and 1.55 μm, and therefore the presence of unreacted hydroxyl groups will lead to serious optical loss. For optimum performance the pendant double bonds should remain unreacted prior to UV writing or exposure. In order to obtain a maximum degree of methacryloylation and double-bond retention various reaction conditions were explored.

In general methacryloylation[24] of an alcohol is performed in the presence of an organic base. In this report, triethylamine was used for this purpose. Our first attempts of methacryloylation involved the use of methacryloyl chloride (MACl). Whilst it proved possible to prepare methacryloylated copolymer by this method[25], the results were not consistent and it proved difficult to isolate the product which varied in nature from a nice pure powder to a contaminated sticky solid. We therefore explored the use of methacrylic anhydride (MAAN) as an alternative acylating agent since this has previously been shown to give better performance and reproducibility[24]. Methacryloylation results obtained using MAAN are summarized in Table 2. All reactions were performed at room temperature. This anhydride, though less reactive than methacryloyl chloride, is often suitable for the preparation of esters when mild conditions are required. From the data in table 2 it is also evident that 70%-HEMA-content polymers methacryloylated well under such conditions. Batches **8d** (10%), **9a**, **9c** (20%), **10a** (34%), **11b-c**, **11e** (47%), **12b-c** (70%) and **13a**(85%) gave high degrees of methacryloylation as well as a high level of double bond retention. As will be seen in Table 2 change of solvent from DMF to DCM also improved the degree of methacryloylation. However a large excess of MAAN had to be used for lower (10-20%) HEMA-content polymers (batches **8d**, **9a**, and **9c**) in order to obtain a high degree of methacryloylation (see Table 2). Use of the anhydride (MAAN) also made product isolation easier. Table 2 also shows that double bonds were retained well during the reaction without requiring the addition of *p*-benzoquinone stabilizer; indeed for many batches, purer polymers were obtained when it was not present.

<Table 2>

Polymer Characterization

Copolymer composition (see Table 1) and the degree of methacryloylation and of double bond retention (see Table 2) were determined by ^{1}H NMR spectroscopy. For low HEMA-content (≤20%) copolymers the integral of the methyl resonance of MMA at δ 3.60 ppm was compared with those for the methylene resonances of hydroxyethyl group of HEMA at about δ 4.11 and 3.84 ppm. However for higher-HEMA-content copolymers (>47 %) resonances of hydroxyethyl group shift to ca. δ 3.65 and 3.90 ppm and thus former of these overlaps with that for the methyl resonance of MMA (at δ 3.60 ppm). In such cases, the composition of the copolymer, and the degree of methacryloylation and of double bond retention after the methacryloylation reaction were determined from the comparison of peak integrals in the ^{1}H NMR spectra[##] (an example of which is shown in Figure 1).

<Figure 1>

The presence of C=C double bonds was confirmed by FT-IR spectroscopy, methacryloylated polymer showing a C=C absorption at 1637 cm^{-1} (see figure 5).

UV absorptivity

In order to modify core and cladding layers of a waveguide by UV writing techniques a polymer should have proper UV absorptivity. Methacryloylated polymer **11e** (having 47%-HEMA-content) was found to have 63% transmission at 244 nm for a 3.7 μm thick film; this is a reasonable absorption for UV laser writing applications. After UV lamp irradiation for 2 h, transmission at 244 nm was reduced to 60%, indicating that crosslinking involving the C=C bonds had occurred (Figure 2).

<Figure 2>

Thermal properties

Thermal behaviour of methacryloylated polymers was investigated by DSC and TGA. Table 3 summarizes the DSC and TGA results. Gradual exothermic behaviour of methacryloylated 47%-HEMA-content polymer was detected together with a sudden drop in heat flow indicating the occurrence of a chemical reaction during heating (Figure. 3). This may be explained by thermal crosslinking of the pendant C=C double bonds. Polymers with more double bonds crosslink more readily at lower temperatures.

<Figure 3>

<Table 3>

The thermal stability of these polymers was investigated by TGA. The copolymer with 10%-HEMA content showed weight loss above 260°C. All other copolymers with higher HEMA-content (34%, 47% and 70%) started to decompose at around 210°C. Figure 4 shows TGA results for batches **8b** (10%) and **12c** (70%).

<Figure 4>

Crosslinking Evidence

The methacryloylated polymers described here experience both thermal and photo-induced-crosslinking[26-28] and are sufficiently reactive to crosslink above 100°C without need for a radical initiator. They additionally have absorptions in the UV region and can be crosslinked using a 254nm low pressure UV lamp.

In order to gain better insight into the behaviour of these polymers, IR (infrared) and solid state ^{13}C CPMAS NMR spectroscopic studies were used to explore the chemical changes involved during the crosslinking process. Initially, methacryloylated P(MMA/MAOEMA) **11e** was exposed under a low pressure mercury UV lamp. The reduction in intensity of the carbon-carbon double bond absorption at 1637 cm^{-1} in the IR spectrum (Figure 5) during this process provides clear evidence that the alkene side chains have been removed during photo-induced crosslinking of the polymer. There was a 38%(±5%) reduction in the intensity of the C=C absorption after 2hrs exposure and after 10 hrs exposure only 12%(±6%) of the double bonds remained in the copolymer.

<Figure 5>

Similar results were obtained during thermal crosslinking of P(MMA/MAOEMA) **11e**. Further support for the loss of alkene side groups has come from solid state ^{13}C NMR spectroscopy (Figure 6). A powder sample of polymer was heated at 140°C for 2h after which time the double bond carbon resonances at δ 136.2ppm ($-\underline{C}{=}CH_2$), 126.4ppm ($-C{=}\underline{C}H_2$) and δ 167.0ppm ($-O\underline{C}({=}O)-$) from the HEMA side chain were found to have disappeared and chemical shifts for the methylene carbon at δ 62.9ppm ($-O\underline{C}H_2CH_2O-C({=}O)-$), the methyl carbon of MMA at δ 55.9ppm ($-C({=}O)-O\underline{C}H_3$) and the methyl carbon at δ 18.4ppm ($-C-C(-\underline{C}H_3)(-C{=}O)-$), had shifted consistent with changes in polymer structure arising from thermal crosslinking.

<Figure 6>

Refractive index studies of unfunctionalized and methacryloylated copolymers

To determine the optimal polymer composition we carried out a study of refractive index versus composition for methacryloylated and unfunctionalized polymer layers. For these measurements all films were between 0.3 ~ 0.4 μm thick, and the error range in refractive index measured by ellipsometry was ± 0.003. For unfunctionalized P(MMA/HEMA) polymers, the refractive index varied between 1.497 and 1.516, depending on the HEMA/MMA composition wheareas that for the methacryloylated polymers ranged from 1.504 to 1.518 (Figure 7). The gradients of the fitted lines were $2.0 \times 10^{-4} (\pm 1.6 \times 10^{-5})$ and $1.5 \times 10^{-4} (\pm 2.7 \times 10^{-5})$ which suggest that methacryloylation of P(MMA/HEMA) has very little effect on the relationship between refractive index and composition. We found, in general, that the variability in refractive index was greater in the methacryloylated layer as would be expected from, for example, the batch-to-batch variation in the degree of methacryloylation. The data from this study led us to adopt 47%-HEMA-composition polymer for waveguide studies. Increased scale and better control of batch processing has resulted in greater reproducibility in composition with better refractive index control, variability being reduced to 0.13%.

<Figure 7>

In an actual waveguide the thermally crosslinked P(MMA/MAOEMA) serves as a core layer. Consequently the photosensitivity of thermally crosslinked P(MMA/MAOEMA) was studied by measuring the refractive index after UV exposure. The refractive index of the P(MMA/MAOEMA) with 47% HEMA content was 1.500(±0.001) and decreased to 1.498 upon heating (i.e thermal crosslinking). After UV laser exposure at an energy fluence of 1.9J/mm^2 the refractive index of the sample increased to 1.512. The Δn (=+0.014) is higher than that achieved in UV-written Ge-SiO$_2$ waveguides and is therefore likely to be sufficient for making a wide variety of UV-written waveguides.

Waveguide fabrication and loss

Using the polymers described here we have fabricated a buried channel waveguide. Silica with a refractive index of 1.457 served as the undercladding layer. Methacryloylated P(MMA/MAOEMA) solution (47% HEMA-content) was spin coated and thermally crosslinked as the core layer. The channel was created by UV writing with a cw frequency doubled argon-ion laser (244nm). The overcladding used was again the same P(MMA/MAOEMA) polymer (47% HEMA-content) which was thermally crosslinked after spin coating.

Using the cut-back technique and end-fibre launching, the propagation loss through the channel waveguides was measured to be 0.41 dB/cm with a coupling loss of ~3 dB at 633nm. Losses at 1053nm and 1310nm were found to be <0.2dB/cm and <1dB/cm respectively. A approximately Gaussian mode profile was obtained at 633nm (Figure 8). A more detailed investigation of the waveguide work is presented elsewhere[29].

<Figure 8>

Conclusions

In this study we have demonstrated the suitability of our methacrylated-based copolymers for the formation of UV laser-written waveguides.

Crosslinking of these polymers using either thermal conditions or uv-irradiation has been demonstrated and is coupled with the disappearance of the pendant double bonds and other structural changes as evidenced by FT-IR, and ^{13}C CPMAS NMR spectroscopic studies.

The UV-induced crosslinking process has been used to write refractive index-based waveguides in this material.

Using a UV writing technique a good quality optical channel waveguide was obtained and the propagation loss through this were measured to be less than 1 dB/cm at wavelengths covering the important near IR telecom bands. The Δn (=0.014) of these materials is higher than that achieved in UV written Ge-SiO_2 waveguides and we conclude that this system is a good candidate for applications in all types of UV written waveguide devices.

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[#]However, as a refree has noted, because of the high degree of conversions in this work gel effects will predominate in determining the outcome of these experiments.

[##]When methacryloylation is not completed a tiny peak arising from the presence of unreacted methylene protons ($-C\underline{H}_2CH_2-OH$) appears at δ 3.84 ppm (as seen in Figure 1); resonances at δ 4.20 and δ 4.35 ppm contain both methacryloylated methylene ($-C\underline{H}_2C\underline{H}_2-OCOC(CH_3)=CH_2$) and unreacted methylene protons ($-CH_2C\underline{H}_2-OH$). Therefore the degree of methacryloylation (x) [equation (i)] can be determined by comparing the integrals of peak at δ 4.20 and δ 4.35 ppm (A) with that of peak at δ 3.84ppm (B) (see Figure 1).

$$\{2(1-x)+4x\}/\{2(1-x)\}=A/B \qquad \text{equation (i)}$$

The composition defined by mole ratio (n) [equation (ii)] can be determined by comparing the integral of unreacted methylene proton peak ($-C\underline{H}_2CH_2-OH$) at δ 3.84 ppm (B) with that of the methyl peak at δ 3.60ppm from MMA (C).

$\{2n(1-x)\}/\{3(1-n)\}=B/C$ equation (ii)

The degree of double bond retention (y) [equation (ii)] was determined by comparing the corrected integrals (i.e. subtracting the portion of unreacted methylene protons) at δ 4.20 and δ 4.35 ppm with those for the vinyl protons at δ 5.65 and δ 6.15 ppm (D).

$Y=D/2[A-\{2(1-x)/(2(1-x)+4x)\}]$ equation (iii)