Polymer 44 (2003) 547–556

polymer

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Synthesis and characterization of a novel derivative of chitosan

W. Ding[a], Qing Lian[b], R.J. Samuels[b], M.B. Polk[a,*]

[a]*School of Textile and Fiber Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, USA*
[b]*School of Chemical Engineering, Georgia Institute of Technology, Atlanta, GA 30332-0295, USA*

Received 4 June 2002; received in revised form 4 November 2002; accepted 5 November 2002

Abstract

The *graft*-copolymer of chitosan with 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl I was synthesized by radical polymerization. *Graft*-copolymerization was carried out under homogeneous conditions with AIBN as initiator and 2 wt% acetic acid as solvent. Homopolymerization of I was also carried out to obtain material for comparative analysis. The resulting chitosan *graft*-copolymers were isolated, purified and characterized with FTIR, NMR, DSC, and TGA. Films were then prepared and characterized by X-ray diffraction, wave guide coupling and infrared dichroism techniques.

Keywords: Chitosan–NLO *graft*-copolymer; Polarized FTIR; NMR

1. Introduction

Chitin, the naturally occurring polysaccharide, is one of the principal ingredients of the carapaces, crusts, and shells of crustacea, such as crabs, lobsters, prawns, and shrimps. It is the second most abundant organic resource on the earth next to cellulose, and the amount of its production is estimated to be several billion tons per year [1].

The molecular structure of chitin is shown in Fig. 1. It is a copolymer of β-(1-4)-D-glucosamine and β-(1-4)-*N*-acetyl-D-glucosamine units with varying composition. The physical properties depend on the distribution of *N*-acetyl groups along the chain and on the average degree of *N*-acetylation. In general, chitin consists mainly of β-(1-4)-2-acetamido-2-deoxy-D-glucose units, and is insoluble in aqueous solutions and common organic solvents. When the degree of *N*-acetylation is less than 50%, the chitin becomes soluble in aqueous acidic solutions and is named chitosan. Chitosan is thus the fully or partially deacetylated product of chitin. Two methods have been developed (homogeneous and heterogeneous) for the alkaline conversion of chitin to chitosan [2–5].

Our objective was to synthesize a *graft*-copolymer of chitosan and 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl (monomer) (I) for testing as a second order non-linear optical material. Our primary objective in exploring the poly[4-(6-methacryloxyhexyloxy)-4′-nitrobenzoyl]-*g*-chitosan (*graft*-chitosan) system was to test the lifetime of NLO activity in a system containing the two types of liquid crystalline moieties. Chitosan has been shown to form liquid crystalline solutions in dilute acetic and formic acids and poly[4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl] [6] (homopolymer) is a thermotropic liquid crystal. Liquid crystallinity has been shown to lead to the enhancement of orientation under certain poling conditions. The bulk material non-linearity will be a function of molecular orientation and symmetry. In order to achieve high macroscopic non-linearities the β groups must be aligned. This is usually achieved by poling. A concern is the well-documented decay in non-linear activity over a period of time. Our objective was to prepare a copolymer of a liquid crystalline non-linear optical moiety, which would be oriented by poling, and the orientation locked in by attachment to a lyotropic liquid crystal. As a result, we would expect to observe a decrease in the rate of decay of NLO activity. In our research, poly[4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl] (II) (Fig. 2) was used as the vinyl polymer grafted onto chitosan for the purpose of developing polymeric non-linear optical materials. Also we proposed to thoroughly characterize the *graft*-copolymer system using FTIR, NMR, DSC, and TGA as well as special techniques available in one of the author’s laboratory for characterizing films by X-ray

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* Corresponding author. Tel.: +1-404-894-2535; fax: +1-404-894-8780.
E-mail address: malcolm.polk@tfe.gatech.edu (M.B. Polk).

0032-3861/03/$ - see front matter © 2002 Published by Elsevier Science Ltd.
PII: S0032-3861(02)00834-0

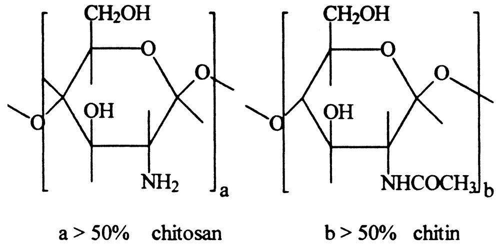

Fig. 1. Molecular structure of chitin and chitosan.

diffraction, wave guide coupling and infrared dichroism techniques.

2. Experimental

2.1. Materials

4-Hydroxybiphenyl, benzoyl chloride, fuming nitric acid, 6-bromo-1-hexanol, 18-crown-6, and methacryloyl chloride were available commercially and were used as obtained. 1,4-Dioxane was dried overnight over calcium hydride and distilled before use. Azobisisobutyronitrile was used as obtained and stored under nitrogen pressure. Chitosan flakes were immersed overnight in distilled water and then dried before use. Other solvents, e.g. pyridine, *n*-butanol, glacial acetic acid, methanol, ethanol, tetrahydrofuran, toluene, and nitrobenzene were used with no further purification.

2.2. Homopolymerization of 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl (I)

The monomer (I) (2 g, 0.0052 mol) was dissolved in 20 ml degassed toluene and 8.54×10^{-3} g (1 mol%) AIBN dissolved in toluene was added. The flask was placed in a 60 °C oil bath and heated for 1 day. During this time, polymer formed and collected at the bottom of the flask. After the required time, the supernatant was poured off and the lower layer mixed with methanol in a blender. The solid polymer was filtered, washed with methanol and vacuum dried. The yield of homopolymer was 1.67 g (84%).

2.3. Graft-copolymerization of chitosan

Chitosan (0.25 g, 6.4×10^{-7} mol) was dissolved in 2 wt% acetic acid (25 ml), and the solution was stirred overnight and filtered through a sintered glass filter before use. The solution, in a 100 ml round-bottomed three-necked flask, was stirred and purged with nitrogen for 30 min. Azobisisobutyronitrile (0.0025 g, 1.52×10^{-5} mol) in the minimum volume of acetone was added, followed by the addition of 0.50 g (1.4×10^{-3} mol) of 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl over 5 min. The reaction was continued at 60 °C for 24 h under nitrogen. The contents of the flask were stirred for an additional 15 min at room temperature, then filtered, and poured into a 100 ml beaker followed by addition of a 10% sodium hydroxide solution with vigorous stirring until the polymer was completely

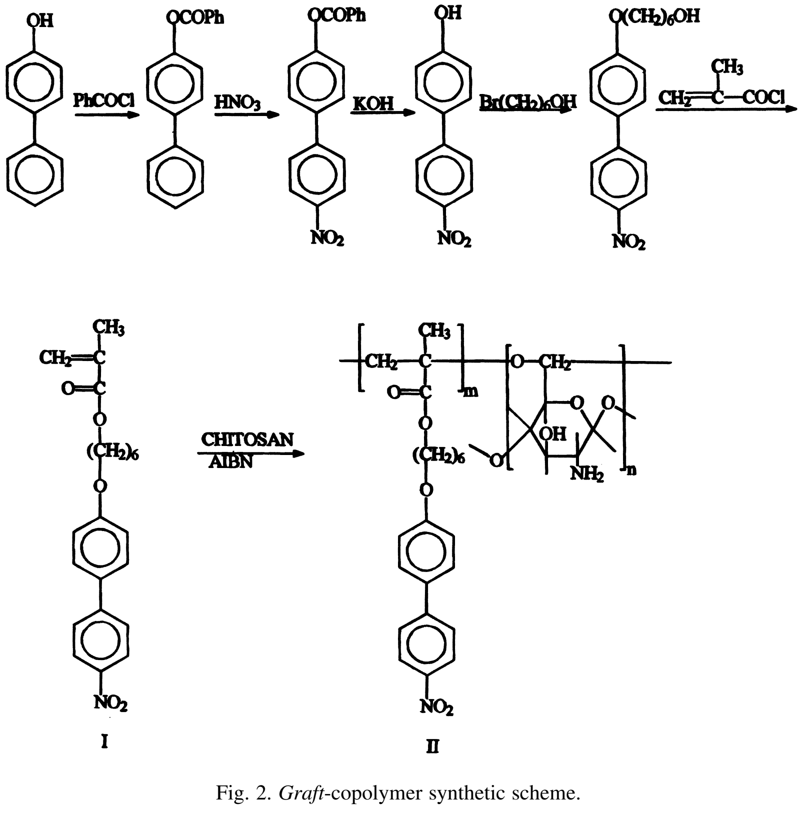

Fig. 2. *Graft*-copolymer synthetic scheme.

Table 1
FTIR spectral assignments of chitosan

Frequency (cm^{-1})	Relative intensity	Assignment
3419.8	Strong	O–H stretching
2940.3, 2868.0	Weak	CH_2 symmetric and asymmetric stretching
1654.1	Medium	Amide I (C=O)
1379.0	Medium	CH_3 symmetric bending
1073.9	Strong	Cellulose–ester type absorption; ring and bridge C–O–C vibrations

precipitated. The gel obtained was extracted with nitrobenzene to remove any poly[4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl] formed during the *graft*-copolymerization. The product was vacuum dried at about 100 °C for 24 h.

2.4. Graft-copolymer film casting

The *graft*-copolymer (II) (0.5 g) was dissolved in 25 ml of 2 wt% acetic acid and stirred overnight. The solution was filtered, spread on a clean glass plate, and left in a dark, dust-free atmosphere at 10 °C for 48–60 h. The film was neutralized by two successive 10 min treatments with 2% aqueous sodium hydroxide solution, after which it could be easily removed from the plate. It was then thoroughly rinsed and air-dried.

2.5. Characterization

Intrinsic viscosities were measured at 25 °C with an Ubbelohde type viscometer with sodium chloride (0.2 M) and acetic acid (0.1 M) as the solvent system for chitosan. The intrinsic viscosities of the homopolymer and *graft*-copolymers were not determined because of the lack of complete solubility in dilute acetic acid and nitrobenzene, respectively. The molecular weight of chitosan was calculated from the Mark–Houwink equation.

Fourier transform IR spectra were obtained with a Perkin–Elmer FTIR 1600 series spectrometer and all samples were prepared as potassium bromide pellets except that chitosan and *graft*-chitosan samples were prepared as films. Film spectra were collected on a Nicolet 60SX FTIR spectrometer at 2 cm^{-1} resolution with a CsI beamsplitter, and TGS detector. One hundred scans were coadded per spectrum. For stretched films, the radiation was polarized using a double wire grid polarizer. Twenty-one polarized spectra were obtained per sample as a function of angle around the film in order to accurately determine both the symmetry axis and the dichroic ratio of each infrared absorption band of interest.

Differential scanning calorimetry (DSC) was performed on a Seiko Instrument DSC 220 °C under a nitrogen atmosphere. Thermogravimetric analysis (TGA) was performed on a Perkin–Elmer TGA 7 Series under a nitrogen atmosphere. A temperature range of 30–700 °C was used in each scan with a scan rate of 15 °C/min.

Proton NMR spectra were obtained with a Varian XL-400 NMR Spectrometer. NMR spectra of the monomer and the homopolymer were obtained in nitrobenzene-d_5 solution, and the NMR spectrum of the *graft*-copolymer was obtained in a 2 wt% acetic acid polymer solution.

The three-dimensional refractive indices of the films were characterized with a prism-wave guide coupler (Metricon PC-2010) at 633 nm. The technique was previously developed and tested on a range of different freestanding and spin coated polymer films [7,8]. In this paper, N_z is the refractive index along the optical symmetry axis, N_y is the refractive index perpendicular to the symmetry axis in the film plane, while N_x is the refractive index normal to the film plane. The birefringence is defined as $\Delta zy = N_z - N_y$, $\Delta zx = N_z - N_x$, $\Delta yx = N_y - N_x$.

Films were characterized using a Rigaku diffractometer with Ni filtered Cu Kα radiation. The diffractometer was operated at 150 mA and 45 kV.

3. Results and discussion

3.1. Preliminary evaluation of chitosan

The percent deacetylation was determined by the base-line method of Roberts and Baxter [9], using the relationship %deacetylation $= 100 - (A1655/A3450)(115)$, where A is the absorbance at the given wavenumber. According to the infrared analysis, the degree of deacetylation of chitosan used in this research was 80%. Chitosan FTIR spectral assignments are shown in Table 1.

The viscosity average molecular weight of chitosan (3.89×10^5 g/mol) was calculated from the Mark–Houwink relationship: $[\eta] = K_m M_v^a$, where $K_m = 8.93 \times 10^{-4}$ dl/g and $a = 0.718$.

The ^1H NMR spectrum of chitosan was recorded in a 2 wt% CD_3COOD solution (Fig. 3). From the NMR spectrum of chitosan, three peaks could be assigned unambiguously. The proton that is most downfield shifted is the proton on the anomeric carbon (at δ 4.9 ppm) and the protons that are present most upfield are the methyl protons (at δ 2.1 ppm) from the acetylated chitosan. The proton appearing at δ 3.2 ppm is that on the carbon bearing the acetamido group. The degree of deacetylation was found to be ca. 77% from NMR analysis.

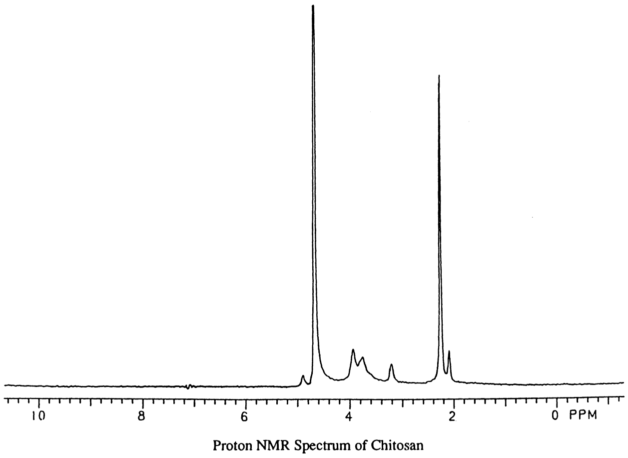

Fig. 3. ^{1}H NMR spectrum of chitosan.

3.2. Synthesis of 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl (I)

The procedure developed by Demartino et al. [10] was used for the synthesis of 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl. ^{1}H NMR, δ ($CHCl_3$, TMS, ppm):1.39–1.56 (middle CH_2), 1.62–1.82 (protons on methylene carbons β to oxycarbonyl and biphenyloxy oxygens), 1.96 (CH_3), 3.96 (protons on methylene carbon α to biphenyloxy oxygen), 4.19 (protons on methylene carbon α to oxycarbonyl oxygen), 6.18, 5.59 (methylene protons of the methacryl group), 6.98 (biphenyl protons ortho to hexyloxy group), 7.58 (biphenyl protons meta to hexyloxy group), 7.68 (biphenyl protons meta to nitro group), and 8.19 (biphenyl protons ortho to nitro group).

3.3. Synthesis of poly[4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl]

Poly[4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl] was synthesized by the AIBN initiated radical polymerization of 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl in toluene. The yield of homopolymer was 84%.

3.4. Fourier transform infrared analysis of poly[4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl]

The infrared spectrum of the homopolymer of 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl is quite similar to that of the monomer, but there are two main differences. The peaks at 1653 and 1636 cm^{-1}, which represent C=C stretching in the monomer, almost disappear in the spectrum of the homopolymer. The other difference is that the peak representing C=O stretching appears at a higher frequency in the homopolymer than in the monomer (1724 cm^{-1}) in Table 2. This is because the carbonyl group in the monomer is conjugated with a C=C, which causes the position of the C=O stretching peak to shift to lower frequency.

Table 2
FTIR assignments of mesogen homopolymer

Peak (cm^{-1})	Assignment
1724.3	C=O stretching
1595.9, 1517.6, 1342.4	N–O stretching
857.1	C–N stretching
1486.3	Aromatic C=C stretching
828.9, 756.9, 735.0	Substituted aromatic C–H bending

3.5. Proton nuclear magnetic resonance analysis of the homopolymer

The proton NMR spectrum of the homopolymer is shown in Fig. 4. The two peaks around 6.00 ppm, which represent olefinic protons almost disappear in the spectrum of homopolymer compared to the monomer spectrum. This demonstrates that the homopolymerization was successful.

3.6. Graft-copolymerization of chitosan with 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl

Since Blair had shown that the heterogeneous *graft*-copolymerization process led primarily to surface grafting, we chose to use the homogeneous *graft*-copolymerization method of Blair [11] for the *graft*-copolymerization of 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl onto chitosan. A series of *graft*-copolymerizations were carried out under the reaction conditions shown in Table 3. When the reaction was complete, the reaction mixture consisted of homopolymer, monomer and *graft*-chitosan. Since nitrobenzene was found to be a solvent for the homopolymer and the monomer, the resulting *graft*-chitosan was isolated by thoroughly washing the residue from the reaction mixture with nitrobenzene to ensure the removal of homopolymer and monomer. The grafting percentage was calculated from the increase in weight of the original chitosan. Clear films were obtained by casting the acetic acid solutions of *graft*-chitosan onto glass plates.

3.7. Fourier transform infrared analysis of graft-chitosan (II)

The FTIR spectra of chitosan, poly[4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl], and chitosan-*g*-poly[4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl] films are shown in Fig. 5 for comparative purposes.

Four additional peaks appear in the FTIR spectrum of chitosan-*g*-poly[4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl] compared to that of chitosan. Additional peaks appear at 1736.0, 1597.8, 1525.4, and 1347.7 cm^{-1}. The three peaks at 1597.8, 1525.4 and 1347.7 cm^{-1} represent the N–O stretching of the nitro group, and the peak at 1736.0 cm^{-1} represents the C=O stretching of the ester group. Compared with the C=O absorption of the monomer at 1712.0 cm^{-1}, the C=O stretching of *graft*-chitosan appears at a higher frequency. The C=O group in *graft*-chitosan is not conjugated

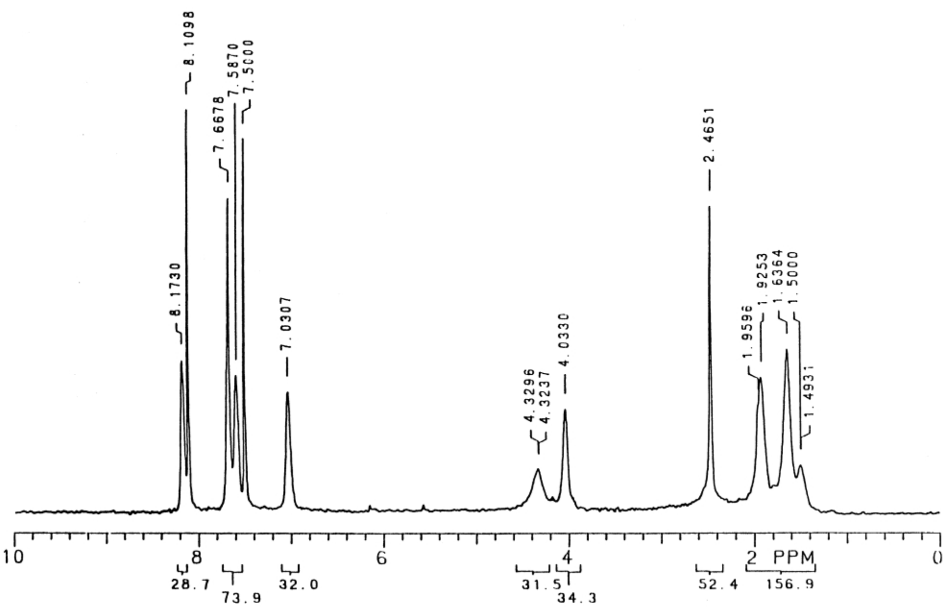

Fig. 4. ^{1}H NMR spectrum of homopolymer.

because of reaction of the monomer carbon–carbon double bond during *graft*-copolymerization, and this causes the C=O stretching peak to shift to higher frequency. This confirms the successful achievement of *graft*-copolymerization.

Fig. 6 shows the FTIR spectra of five samples from different *graft*-copolymerization runs using different proportions of initiator and monomer. It is clear that the C=O stretching peak at 1736 cm^{-1} of sample 4 is more intense than that of the other samples. This indicates that sample 4 has a higher grafting percentage, and this result is consistent with the grafting ratios obtained from the weight increase as shown in Table 3.

3.8. Proton NMR analysis of graft-chitosan

The ^{1}H NMR spectrum of *graft*-chitosan (Fig. 7) was recorded under identical conditions to that of chitosan (Fig. 3). Comparison of the integration of the peaks in the aromatic region to that of proton 1 (δ 5.1 ppm) or 2 (δ 3.4 ppm) provided the grafting percentage. Using the area under proton 2 (the proton bonded to the carbon also bearing the acetamido group) as the internal standard the grafting percentage was determined to be approximately 5%. The difference in grafting% shown in Table 2 and that obtained from ^{1}H NMR may be the result of the treatment required to solubilize the *graft*-chitosan sample for NMR analysis. Although the bulk *graft*-chitosan samples show higher grafting percentages, on dissolving the *graft*-chitosan samples in acetic acid solution, some of the grafts are hydrolyzed.

3.9. Differential scanning calorimetry of chitosan, homopolymer and graft-chitosan

The DSC curves of chitosan and *graft*-chitosan show an

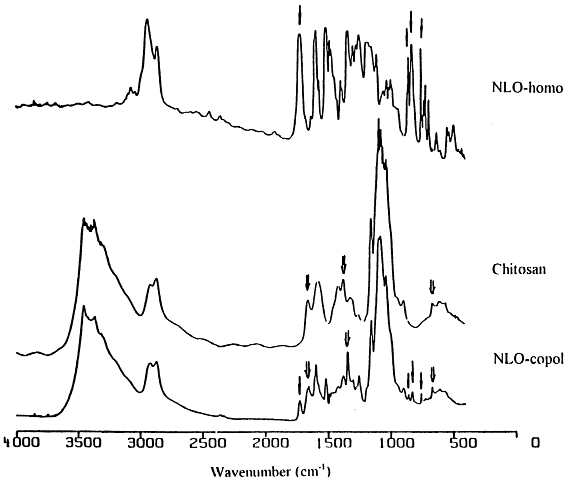

Fig. 5. FTIR spectra of NLO homopolymer, chitosan, and NLO copolymer.

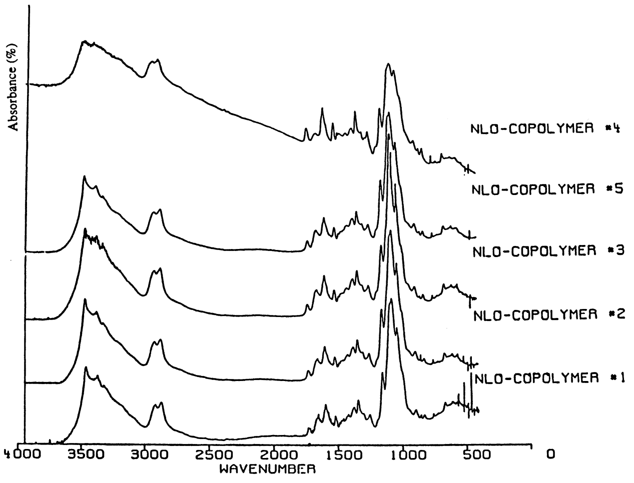

Fig. 6. FTIR spectra of products from five *graft*-copolymerization runs.

Table 3
Graft-copolymerization conditions and results

Sample no.	Chitosan (g)	Mesogen (g)	AIBN (g)	2 wt% CH_3COOH (ml)	Temperature (°C)	Time (h)	*Graft*-chitosan (g)	Grafting (%)
1	0.25	0.5	0.0025	25	60	24	0.2665	10.6
2	0.25	0.5	0.005	25	60	24	0.282	12.8
3	0.25	0.5	0.0075	25	60	24	0.301	20.4
4	0.25	0.5	0.01	25	60	24	0.359	43.6
5	0.25	0.5	0.0125	25	60	24	0.3055	22.2

important qualitative difference. As shown in Fig. 8C, the endothermic peak at 100.4 °C of *graft*-chitosan is due to liberation of water contained in chitosan compounds. Two exothermic peaks, which appear at 304.4 and 347.3 °C, respectively, correspond to thermal degradation of the chitosan main chain and the side chain of the appended graft. The first degradation peak appears at a temperature very close to the degradation temperature of chitosan as shown in Fig. 8A, while the second one is almost the same as the degradation temperature of the homopolymer (shown in Fig. 8B).

3.10. Thermogravimetric analysis

The thermal behavior of *graft*-chitosan is very different from that of chitosan as can be observed in Fig. 9B. While Chitosan has two main decomposition stages with one starting at 238 °C and another starting at around 320 °C, the *graft*-chitosan exhibits three decomposition stages. They start at around 216, 338.6 and 510.4 °C. When the temperature is above 500 °C, their degradation behavior differs significantly. The degradation rate of *graft*-chitosan is much higher than that of chitosan, and is more like that of homopolymer as shown in Fig. 9A.

3.11. Examination of homopolymer films

3.11.1. FTIR spectroscopy

The FTIR spectrum of the mesogen homopolymer is shown in Fig. 5.

3.11.2. Three dimensional refractive index

The mesogen homopolymer film is rough, brittle and the surface is not uniform. The 'knee' in the intensity-angle curve from the wave guide coupler is hard to determine, and the sample is not thin enough to use mode analysis. Therefore, the refractive indices determined by knee analysis shown below are approximate values.

$$N_p = 1.6627, \qquad N_t = 1.6654, \qquad N_{av} = 1.6636.$$

It is seen that the mesogen homopolymer film is essentially optically random in three dimensions, and its average refractive index is higher than the 1.53 [7,8] reported for chitosan film.

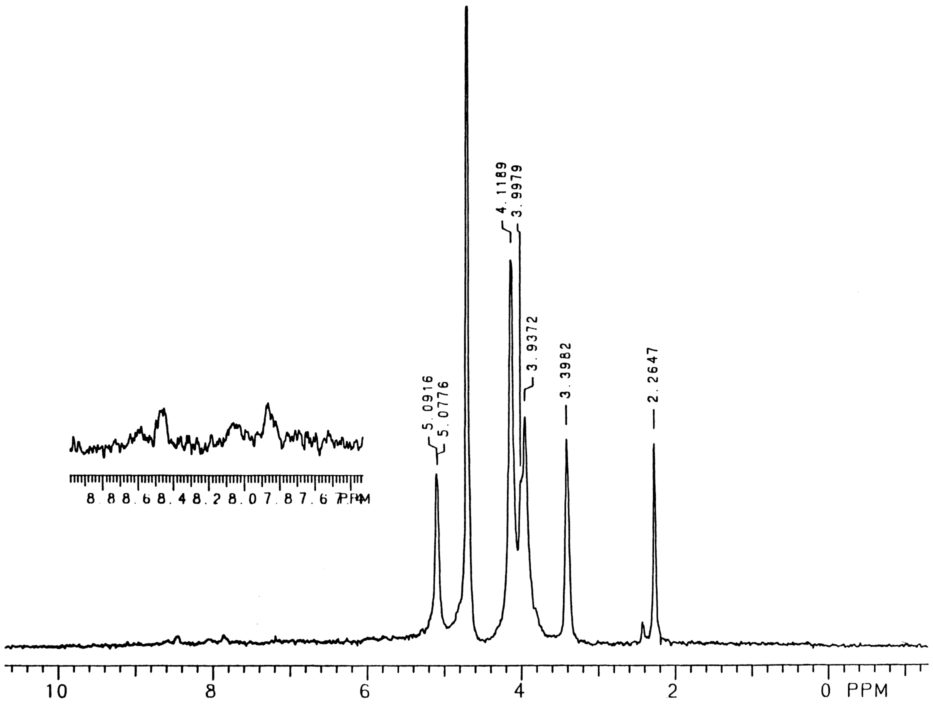

Fig. 7. ^{1}H NMR spectrum of chitosan *graft*-copolymer.

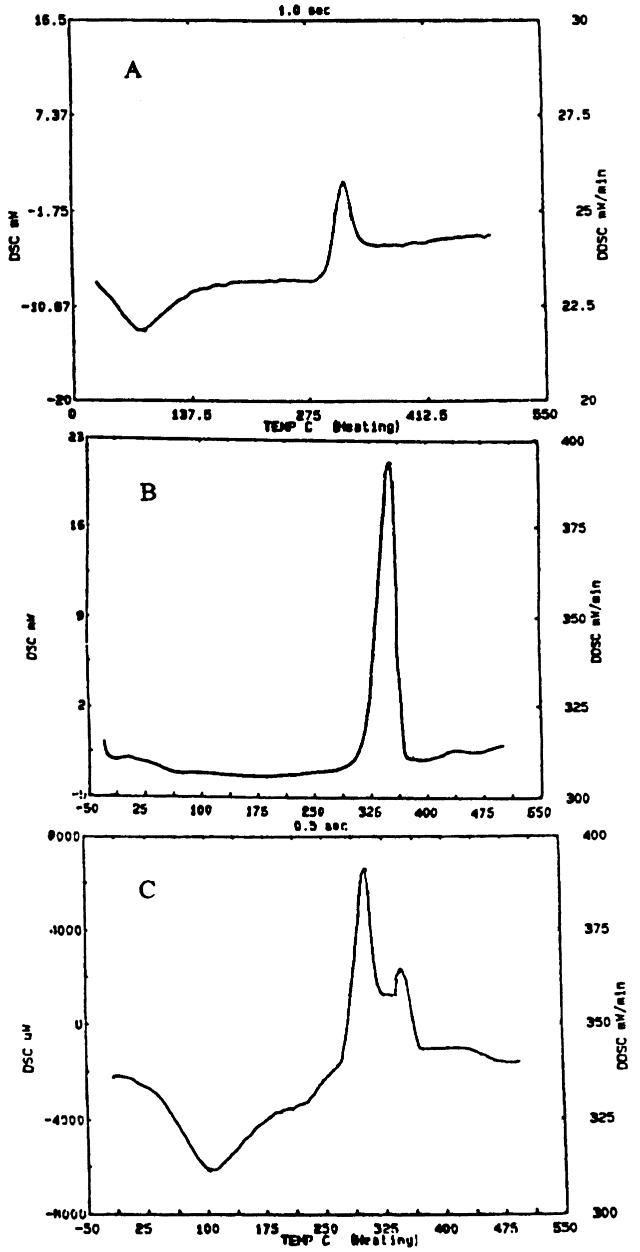

Fig. 8. (A) DSC of chitosan; (B) DSC of mesogen homopolymer; (C) DSC of chitosan *graft*-copolymer.

3.11.3. X-ray diffraction

The radial X-ray diffraction pattern scan of this rough sample is shown in Fig. 10. It is seen that there is a broad peak at $2\theta = 20°$, and a tiny hump at $2\theta = 7°$. Thus the mesogen homopolymer is amorphous.

3.12. Characterization of NLO–mesogen chitosan copolymer film

Chitosan and mesogen–chitosan copolymer but not mesogen homopolymer can dissolve in acetic acid/water solution. But after storing in air for several months, the copolymer did not dissolve in the acetic acid/water solution completely. Fig. 11 shows the infrared spectrum of the undissolved portion from the copolymer/acetic acid solution, and pure homopolymer. It is seen that the undissolved portion has the same infrared spectrum as the homopolymer. So some of the copolymer degraded to form homopolymer during dissolution. This implies that degradation takes place in the copolymer when it is in the acetic acid/water environment and the mesogen–chitosan copolymer in the acetic acid/water environment is not stable.

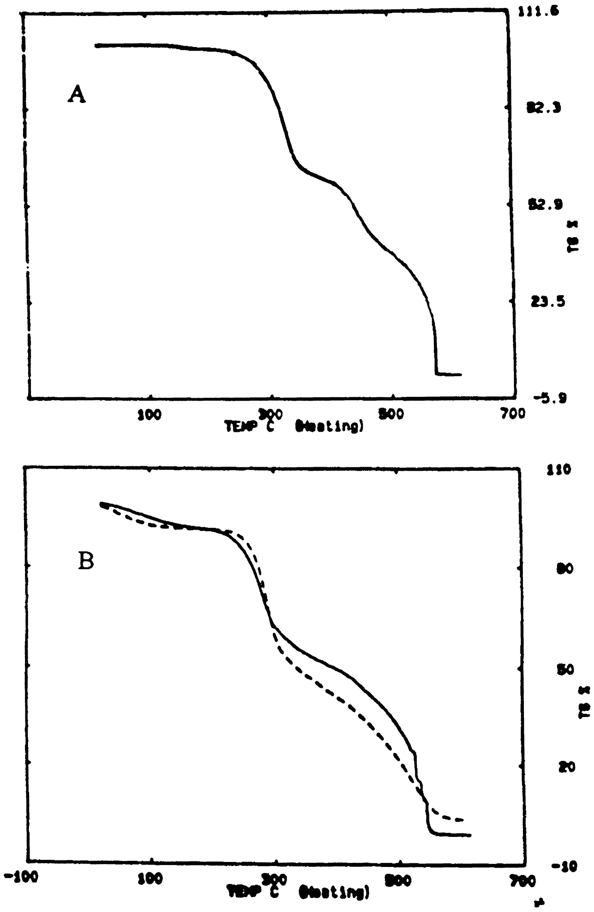

Fig. 9. (A) TGA of homopolymer; (B) TGA of chitosan (- - -) and chitosan *graft*-copolymer (—).

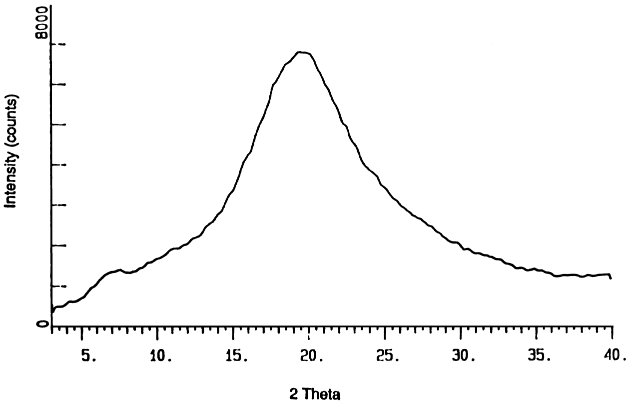

Fig. 10. X-Ray diffraction scan of mesogen homopolymer.

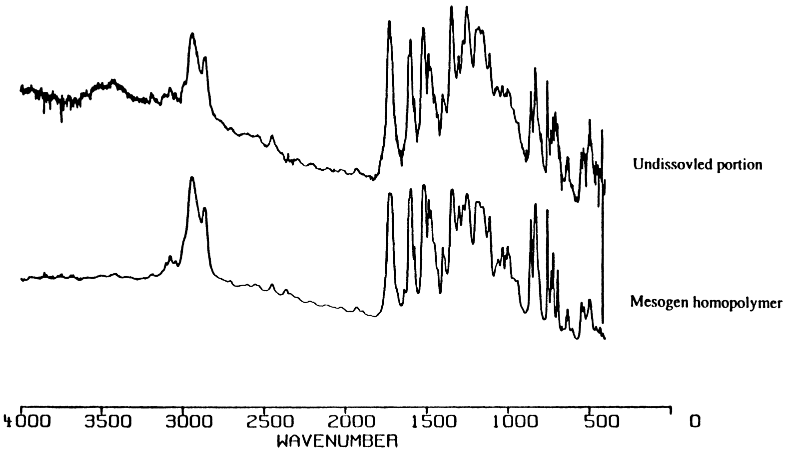

Fig. 11. FTIR spectrum of mesogen homopolymer and undissolved material in acetic acid/water.

Copolymer film can be cast from acetic acid/water solution. This as-cast film, like as-cast chitosan film [11] is in its acid form. After basic washing, this copolymer film is converted back to its original form as shown by FTIR analysis. The effect of washing with sodium methoxide/methanol on the infrared spectra of copolymer film is shown in Fig. 12.

The effect of the washing procedure on the refractive indices of the copolymer film is shown in Table 4. It is seen in Table 4 that the refractive index of the copolymer film increases after washing; the as-cast copolymer film and base washed copolymer film behave similarly as as-cast and base washed chitosan film; and the unstretched copolymer film is optically random in the plane.

3.13. Identification of the unique bands in the copolymer film

In order to trace the orientation behavior of chitosan and mesogen separately in the NLO–chitosan copolymer simultaneously by infrared spectroscopy, we have to identify the unique infrared bands which represent only chitosan or mesogen. Fig. 5 shows the comparison of the infrared spectra of chitosan, mesogen homopolymer and NLO–mesogen chitosan copolymer. It is found that the bands only representing chitosan are 1653, 1379 and 660 cm^{-1}; the bands only representing mesogen are 1724, 857, 829 and 756 cm^{-1}.

Thus chitosan and the mesogen are found to have their own unique bands in the infrared spectrum of the *graft*-copolymer. These bands could now be used to follow the separate behavior of chitosan and mesogen in the copolymer simultaneously.

3.14. Deformation of the copolymer film

The copolymer film can swell in water easily because 95% of the copolymer is chitosan. It cannot, however, swell as much as chitosan in water [7] due to the mesogen unit present. A higher film extension can be obtained by stretching the copolymer film in water rather than in air. The stretching procedure is similar to that of chitosan [7,8].

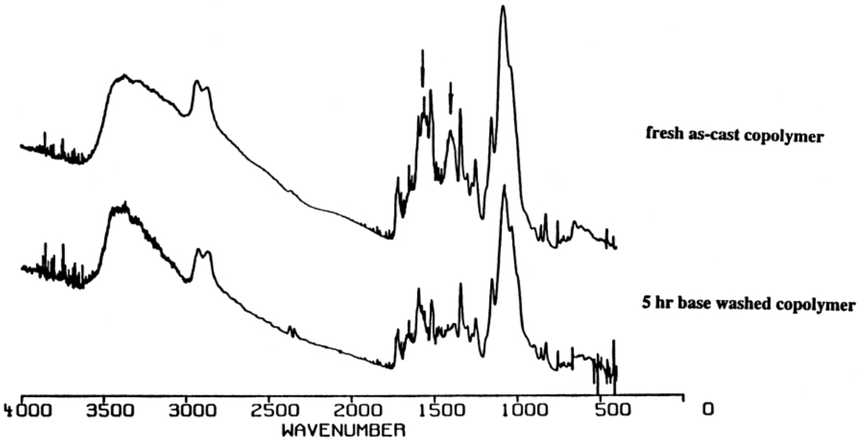

Fig. 12. Effect of alkaline wash on the FTIR spectrum of the chitosan *graft*-copolymer.

Table 4
Effect of washing procedures on the refractive indices of chitosan *graft*-copolymer

Sample	Refractive index		
	N_p	N_t	N_{av}
As-cast	1.5371	1.5234	1.5325
Washed form	1.5465	1.5306	1.5412

Because of the limited amount of the NLO–mesogen chitosan copolymer sample, only one stretched copolymer film was obtained. The extension was 31%.

3.15. Refractive index and birefringence of the copolymer film

Three-dimensional refractive indices were measured for this stretched copolymer film. Also the effect of the drying time in air on the refractive indices was investigated and shown in Table 5.

It is seen that the three dimensional refractive indices increase with drying time in air. However, the birefringence remains constant with drying time in air. This is a similar behavior to that observed for chitosan films [8] and is due to the lower refractive index water slowly evaporating out of the copolymer film during air-drying.

3.16. Infrared dichroism

The infrared dichroism was measured on the stretched copolymer film by the polarized infrared method and the results are shown in Fig. 13. The dichroic ratio, symmetry axis, and band character of each characteristic band are shown in Table 6 and the polarized spectrum in Fig. 13. A dichroic ratio of 1.0 indicates random orientation. Bands with dichroic ratio values greater than 1.0 are defined as π bands, which show increasing values with increasing orientation. Bands with dichroic ratios less than 1.0 are defined as σ bands, which show decreases in magnitude with increasing orientation.

The character of the bands which only belong to chitosan are consistent with those in chitosan films [8,12]. The chitosan backbone molecules are seen to align along the symmetry axis (draw direction) since the measured symmetry axis values obtained from the unique 1653, 1379 and 660 cm^{-1} chitosan bands are close to 0°.

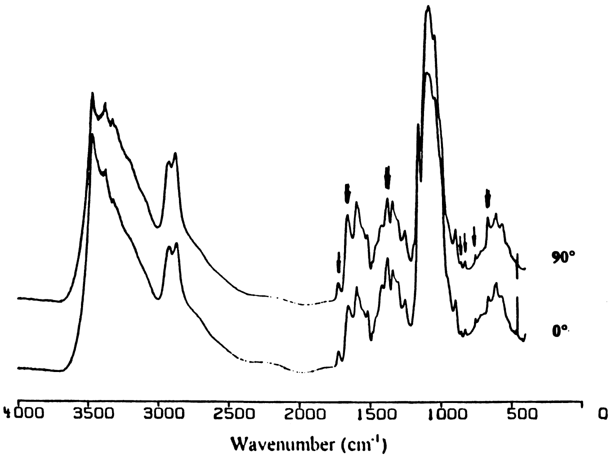

Fig. 13. Infrared dichroism of stretched chitosan *graft*-copolymer film.

However, for the bands that belong to the mesogen graft, the magnitude of the dichroic ratios are very close to the random orientation value of 1.0, even though all of them seem to be π bands with respect to the stretching direction. Because of the low extension of the copolymer sample available, it cannot be clearly concluded how the mesogen molecules would behave at higher extensions. However, compared with the main chain chitosan, the mesogen graft in the film seems to be randomly oriented with respect to the stretching direction.

The importance of these results is that they show that during deformation the molecular organizational changes of each of the components of the copolymer, mesogen graft and chitosan backbone, can be isolated. This thus now makes possible the identification, specifically and quantitatively, of the influence of mesogen orientation on the non-linear optical response to electrical and magnetic fields.

4. Conclusions

The grafting of a non-linear optical mesogen onto chitosan has been successful and the products quantitatively analyzed. The following conclusions can be drawn from the results:

1. The mesogen monomer, 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl was synthesized by applying the procedure of Leslie et al. [10]. The synthesis was confirmed through FTIR, DSC and NMR analysis.

Table 5
Effect of drying time in air on the chitosan *graft*-copolymer refractive indices

Sample	Refractive index				Birefringence		
	N_z	N_y	N_x	N_{av}	Δzy	Δzx	Δyx
Two days after stretched	1.5462	1.5350	1.5291	1.5368	0.0112	0.0171	0.0059
Two months after stretched	1.5515	1.5402	1.5355	1.5424	0.0113	0.0160	0.0047

Table 6
Dichroic ratio, symmetry axis, and band character of bands in Fig. 13

Band (cm^{-1})	Dichroic ratio	Symmetry axis (degrees)	Band character
1724 (mesogen)	1.015	13	π[a]
1653 (chitosan)	0.699	2	σ
1379 (chitosan)	1.190	2	π
857 (mesogen)	1.080	− 19	π[a]
828 (mesogen)	1.038	81	π[a]
756 (mesogen)	1.100	84	π
660 (chitosan)	0.568	4	σ

[a] The magnitude of the dichroic ratio is too close to 1.0 to characterize the bands confidently as π bands.

2. The non-linear optical homopolymer of 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl was successfully synthesized. The synthesis was confirmed through FTIR and NMR analysis.
3. The mesogen homopolymer film was shown to be almost optically random in three dimensions.
4. The mesogen homopolymer is amorphous.
5. The *graft*-copolymerization of 4-(6-methacryloxyhexyloxy)-4′-nitrobiphenyl onto chitosan was successful. Evidence of grafting has been obtained by FTIR, NMR, DSC and TGA analysis.
6. The mesogen–chitosan copolymer in an acetic acid/water environment is not stable.
7. As-cast copolymer film and base washed copolymer film behave similarly as as-cast and base washed chitosan film.
8. The unstretched copolymer film is optically random in the plane.
9. Chitosan and mesogen are found to have their own unique bands in the infrared spectra of the copolymer, which can be used to trace the separate behavior of chitosan and mesogen in the copolymer simultaneously.
10. The three dimensional refractive indices of the copolymer film increase with time in air, but the birefringence remains constant due to water evaporation.
11. On stretching, the chitosan chains align along the stretching direction, but the mesogen chains are random to the stretching direction.

Acknowledgements

The authors wish to thank the Department of Commerce National Textile Center for support of this work.

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