

PREPARATION OF POLYMERS CONTAINING PENDANT QUINONOID GROUPS AND THEIR PHOTO-CROSS-LINKING BY IRRADIATION WITH VISIBLE LIGHT

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(Received April 23, 1986)

Summary

New photosensitive polyurethanes with quinonoid groups as pendant groups were prepared by polyaddition reactions of 3-(*p*-benzoquinonylthio)-1,2-propanediol with diisocyanates (diphenylmethane-4,4'-diisocyanate, 2,4-tolylene diisocyanate or hexamethylene diisocyanate) in the presence of di-*n*-butyltin dilaurate catalyst. The structures of these polyurethanes were characterized by their UV, IR and nuclear magnetic resonance spectra and the contents of quinonoid groups in the polyurethanes were determined by their elemental analyses. These polymers have an absorption maximum at about 430 nm, and upon irradiation with visible light ($\lambda > 370$ nm) they become insoluble in organic solvents.

1. Introduction

Quinone-containing polymers are of great interest because when quinones are attached to macromolecules they show new, distinctive and sometimes unusual properties as exemplified by changes in reactivity, electrochemical behaviour and catalytic properties.

In the studies described in our previous paper [1], *p*-benzoquinone was photochemically introduced into the side chains of poly(methyl methacrylate). In separate work [2], *p*-benzoquinonylthio groups were introduced into the side chains of poly(glycidyl methacrylate) and poly(hydroxyethyl methacrylate-methyl methacrylate) by chemical reaction. In these experiments the main difficulties were the achievement of high reaction yields and the avoidance of side reactions, particularly cross-linking. An increase in the content of functional groups was essential to obtain higher photosensitivity and higher resolution for practical uses.

In this paper, polyaddition reactions of a dihydroxy compound, 3-(*p*-benzoquinonylthio)-1,2-propanediol (Q-s-G), with several kinds of diisocyanates were carried out in order to obtain polymers with a high content of pendant quinonoid groups. Notable advantages of this method were

that the starting material can readily be prepared by the reaction of *p*-benzoquinone and 3-mercapto-1,2-propanediol under mild reaction conditions and that there were no side reactions. The characterization and photochemical behaviour of the resulting polymers are described below.

2. Experimental details

2.1. Synthesis of 3-(*p*-benzoquinonylthio)-1,2-propanediol

To a solution of *p*-benzoquinone (10.8 g, 0.1 mol) in ethanol (450 ml) was added 3-mercapto-1,2-propanediol (5.4 g, 0.05 mol) in one portion. After stirring overnight at room temperature, the solvent was removed by vacuum evaporation and the residue was recrystallized from ethanol. (Yield, 5.8 g; melting point, 139 - 141 °C. IR (KBr): 3350 (O—H), 1660 and 1640 (C=O) cm^{-1} . UV (in tetrahydrofuran (THF)): $\lambda_{\text{max}} = 422 \text{ nm}$ ($\log \epsilon = 3.46$). Proton nuclear magnetic resonance (^1H NMR) (in deuterated dimethyl sulphoxide ($\text{DMSO-}d_6$)): δ 6.5 - 6.8 (quinonoid ring), δ 2.90, 3.45, 3.70 and 4.70(t), 5.10(d) (hydroxyl).)

2.2. Polyaddition reaction of 3-(*p*-benzoquinonylthio)-1,2-propanediol with diisocyanates

1.07 g (5×10^{-3} mol) Q-s-G was reacted with 1.25 g (5×10^{-3} mol) diphenylmethane-4,4-diisocyanate (MDI) in dimethyl formamide (DMF) in the presence of di-*n*-butyltin dilaurate catalyst. After stirring for 1 h in an ice bath and overnight at room temperature, the reaction mixture was poured into methanol to precipitate the polymer. The polymer obtained was reprecipitated from THF-MeOH and then dried under vacuum. (Yield, 1.70 g (73%).)

A similar procedure was carried out with 2,4-tolylene diisocyanate (TDI) and hexamethylene diisocyanate (HDI) instead of MDI. In the case of the reaction with TDI, THF was used instead of DMF. In the case of the reaction with HDI, the polymer was precipitated by pouring the reaction mixture into water and then dried under vacuum in an oven at 40 °C.

2.3. Photoirradiation and measurements

The photoirradiation and measurements were performed as described in the previous papers [1, 2]. Elemental analysis was carried out by the use of a Yanaco MT-3 CHN Corder.

3. Results and discussion

A dihydroxy compound containing the *p*-benzoquinonylthio group can readily be prepared under mild reaction conditions as described in Section 2. The presence of the primary and secondary hydroxyl groups was confirmed by the characteristic peaks at 5.10 ppm (doublet) and 4.70 ppm (triplet) respectively in the ^1H NMR spectrum. Both peaks disappeared on addition of a small amount of D_2O and a new peak due to HOD appeared at 3.90 ppm.

The polyaddition reaction of this dihydroxy compound with diisocyanates such as TDI, MDI and HDI in the presence of di-*n*-butyltin dilaurate catalyst gave dark-yellow polymers. Tables 1 and 2 list the molecular weights and the spectral data of the obtained polymers respectively. Table 3 lists the results of elemental analysis. The molecular weights of the polymers could be controlled by varying the conditions of the polyaddition reaction, *i.e.* the mole ratio of hydroxyl to isocyanato groups, although the data are not shown. The formation of the urethane linkage was confirmed by IR spectral data: the presence of the peaks at 1710 - 1730 (COO) and 3320 (NH) cm^{-1} , and the absence of a peak at 2250 (N=C=O) cm^{-1} .

Figure 1 shows UV spectra of the polymer solutions in THF. The concentrations of all the polymer solutions were adjusted to 5×10^{-4} unit mole l^{-1} , assuming that Q-s-G~TDI, Q-s-G~MDI, and Q-s-G~HDI are the repeating units of the corresponding polymers. The characteristic second π - π^* absorption band [3, 4] of the *p*-benzoquinonylthio group was observed in all the polymers and the apparent extinction coefficients were

TABLE 1
Molecular weights^a of the polymers

| Polymer | Mn | Mw | Mw/Mn |
|--------------|-------|-------|-------|
| P(Q-s-G~TDI) | 4000 | 6400 | 1.60 |
| P(Q-s-G~MDI) | 6900 | 12500 | 1.81 |
| P(Q-s-G~HDI) | 11500 | 21400 | 1.86 |

Mn, number average molecular weight; Mw, weight average molecular weight.

^aBased on the polystyrene calibration curve.

TABLE 2
Spectral data for the polymers

| | UV ^a λ_{max} (nm) (log ϵ) | IR (cm^{-1}) | ¹ H NMR ^b δ (ppm) |
|--------------|--|---|---|
| Q-s-G | 422 (3.46) | 3350, ^c 1660, 1640, ... | 6.50, 6.77, 2.90, 3.45, 3.70, 4.70, 5.10 |
| P(Q-s-G~TDI) | 417 (3.40) ^d | 3320, 1730, ^e 1660, 1640, ... | 9.70, 9.00, 7.50, 7.10, 6.90, 5.30, 4.45, 2.20 |
| P(Q-s-G~MDI) | 415 (3.43) ^d | 3320, 1730, ^e 1660, 1640, ... | 9.50, 7.0 - 7.3, 6.70, 4.35, 4.05, 3.75, 3.20 |
| P(Q-s-G~HDI) | 417 (3.36) ^d 360 sh | 3330, 1710, ^e 1660, 1640, ... | 6.6 - 6.8, 7.10, 4.10, 2.7 - 3.2, 1.22 |

^aIn THF.

^bIn DMSO-*d*₆.

^cKBr disk.

^dCalculated by assuming Q-s-G~TDI, Q-s-G~MDI and Q-s-G~HDI to be repeating units in the corresponding polymers.

^eIn film.

TABLE 3
Elemental analysis

| | Calculated (%) | | | Found (%) | | |
|--------------|----------------|-------|------|-----------|-------|------|
| | H | C | N | H | C | N |
| Q-s-G | 4.70 | 50.46 | — | 4.66 | 50.20 | — |
| P(Q-s-G~TDI) | 4.15 | 55.66 | 7.21 | 4.16 | 54.74 | 7.60 |
| P(Q-s-G~MDI) | 4.34 | 62.06 | 6.03 | 4.25 | 61.16 | 5.73 |
| P(Q-s-G~HDI) | 5.80 | 53.39 | 7.32 | 6.06 | 53.50 | 6.97 |

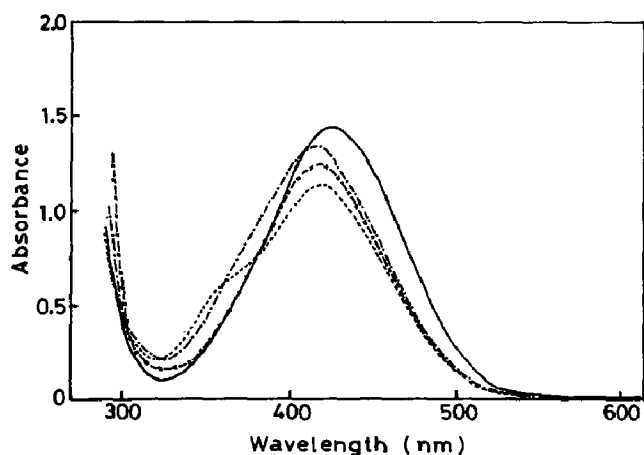
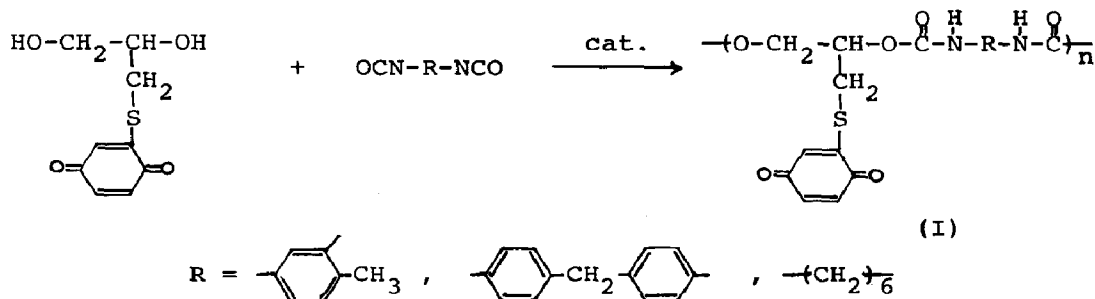


Fig. 1. UV spectra of the polymers in THF: —, 5×10^{-4} M Q-s-G; - - -, 5×10^{-4} units mol $^{-1}$ P(Q-s-G~MDI); - · - ·, 5×10^{-4} units mol $^{-1}$ P(Q-s-G~TDI); · · · ·, 5×10^{-4} units mol $^{-1}$ P(Q-s-G~HDI).

almost the same as that of Q-s-G. It may therefore be concluded that the expected structure (I) of polyurethanes containing *p*-benzoquinonylthio groups was formed without any significant side reaction.



The photochemical behaviour of these polymers was investigated. In Fig. 2 the UV spectral change of P(Q-s-G~MDI) film upon irradiation was compared with that of the blended film of P(Q-s-G~MDI) and poly(vinyl acetate). In the former film, a slight red shift of the second $\pi-\pi^*$ absorption

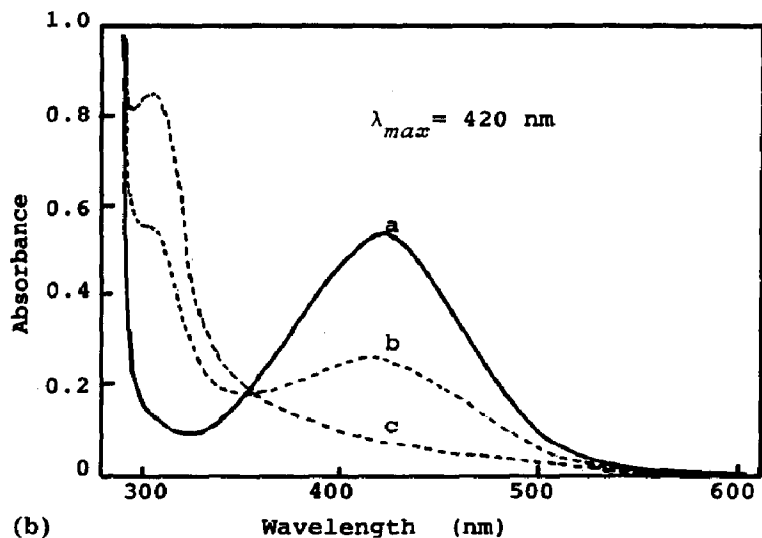
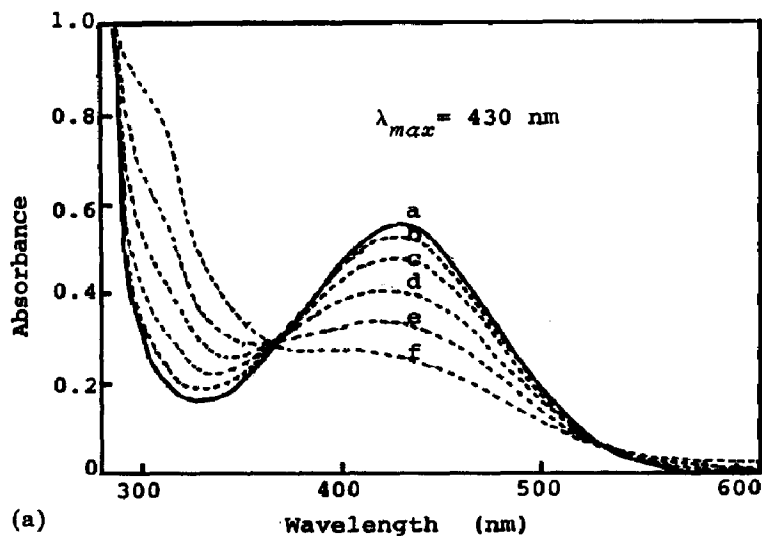


Fig. 2. UV spectral changes of polymer films upon irradiation with a medium pressure mercury arc lamp. (a) P(Q-s-G~MDI) film; (b) P(Q-s-G~MDI) plus poly(vinyl acetate) film. Irradiation time (in minutes): curves a, 0; curves b, 0.5; curves c, 2; curve d, 5; curve e, 10; curve f, 20.

band was observed and its photoreaction was much slower than that of the latter, suggesting the existence of some interaction between the adjacent quinones which may cause the deactivation of the excited quinones. The changes in the features of the UV spectra of the P(Q-s-G~MDI) film were somewhat different from those of the film blended with poly(vinyl acetate), also suggesting the occurrence of some other reactions, *e.g.* dimerization, besides hydrogen abstraction. It has been reported that a number of *p*-benzoquinones, particularly those which are alkyl substituted, dimerize on

UV irradiation in the solid state and in solution [5 - 7]. Ellis and Jones [8] also reported dimerization of 2-methoxy- or 2-ethoxy-substituted naphthoquinone upon irradiation with UV light.

Furthermore, these *p*-benzoquinonylthio-group-containing polyurethanes were insoluble in THF after irradiation. A possible photochemical reaction responsible for insolubilization is the hydrogen abstraction of excited quinonoid groups, as suggested for the photo-cross-linking of poly-(methyl methacrylate). Another possible reaction is the intermolecular dimerization of *p*-benzoquinonylthio groups, and this possibility is supported by the observation of a high photo-cross-linking efficiency in spite of their slow photoreaction.

A preliminary test of the polyurethane films for photoresist was carried out by exposing the spin-coated polymer films through a chrome mask (MK 0208-A-B) and then developing in THF. Generation of fine relief images was observed by the use of an Olympus MF optical microscope. More detailed studies of the photochemical behaviour of these *p*-benzoquinonylthio-group-containing polyurethanes are now in progress.

In conclusion, new photosensitive polymers with a high content of pendant quinonoid groups can be synthesized by polyaddition reaction without the occurrence of any significant side reaction. *p*-Benzoquinonylthio was found to be one of the promising visible-light-sensitive functional groups for photo-cross-linking because of its strong second $\pi-\pi^*$ absorption band in the 350 - 500 nm region. It enables an Ar⁺ laser (488 nm) to be used as an energy source for writing. A wide variety of properties are expected to be obtained on varying the molecular weights or backbone structures of the *p*-benzoquinonylthio-group-containing polyurethanes.

Acknowledgment

This work was supported in part by a Grant-in-Aid for scientific research (No. 60550647) from the Ministry of Education of Japan.

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