Synthesis of New Photochromic Polymers Based on Phenoxynaphthacenequinone

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ABSTRACT: Photochromic compounds of the phenoxynaphthacenequinone type have been incorporated chemically in three polymers: polystyrene, poly(methyl methacrylate), and polysiloxane, overcoming grave synthetic problems due to the presence of the quinone group. Contents of up to one photochromic unit per polymer unit could be obtained without impairing the photochromism of the polymers. Interconversion of the two modifications of the photochrome takes place photochemically but not thermally and is completely reversible, both in the free and in the incorporated photochrome.

Introduction

Photochromism of certain derivatives of naphthacenequinone is due to the photoinduced isomerization of the yellow *p*-quinone form to the *ana*-quinone orange-colored form[1] (Scheme I).

This conversion can be induced by UV light at up to 405 nm.[2] The reverse reaction "ana" into "trans" takes place by irradiation with visible light.

The most significant feature of this material is its low fatigue. The above cycle can be repeated even 500 times without loss of material. Another important feature is that the rate of the thermal reaction "ana" → "trans" is negligible[2] at room temperature. Fulgides have similar properties,[3a] while spirooxazines show low fatigue but undergo rapid thermal equilibration at room temperature.[3b]

Photochromic polymers, i.e. polymers which contain photochromic groups as part of the macromolecule, are materials of significant scientific and technological interest.[3c] Such a structure allows incorporation of a very high content of photochrome in a polymer, approaching 100%; i.e. each structural unit of the polymer contains the photochromic group. Properties of such polymers can be substantially different from the properties of the same polymers containing photochromic molecules as a solute. Moreover, the concentrations of the photochrome in such solutions are limited.

In the present paper we report the synthesis and the absorption spectra of new photochromic polymers containing phenoxynaphthacenequinone as a photochromic side group.

In order to prepare such a polymer one has to synthesize a phenoxynaphthacenequinone which could be connected to a polymer or could be polymerized. This material should fulfill two requirements: (1) The photochromic properties should remain largely unchanged. (2) It should have good solubility in organic solvents in which purification of the polymer is usually performed. Two different derivatives, A and B, of 6-phenoxy-5,12-naphthacenequinone were prepared (Chart I).

Scheme I
Photochromic Transformation of Naphthacenequinone

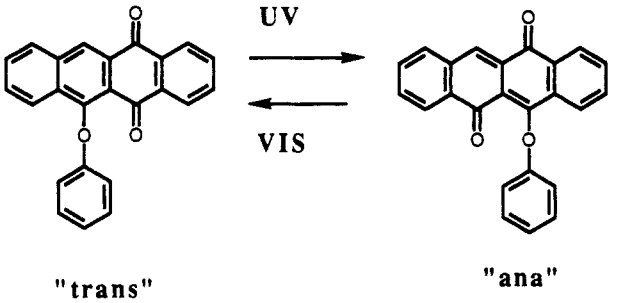
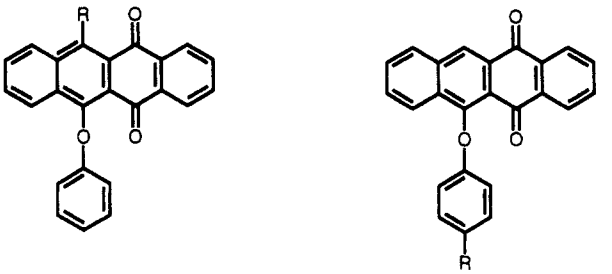


Chart I
Derivatives of 6-Phenoxy-5,12-naphthacenequinone



A B

Experimental Section

Chemicals. The following chemicals were used without further purification: 1,4-naphthoquinone (Merck), 1-naphthol (Fluka), phthalic anhydride (Merck), 3-amino-1-propanol (Fluka), allylamine (Fluka), 4-hydroxyphenol (Fluka), L-tyrosine (Sigma), acryloyl chloride (Fluka), 6-aminohexanoic acid (Merck), 10-undecenoic acid (Fluka), *N*-hydroxysuccinimide (Aldrich), *N,N'*-dicyclohexylcarbodiimide (Merck), di-*tert*-butyl dicarbonate (Fluka), phosphorus pentachloride (Fluka), sodium dithionite (Merck), styrene (Merck), methyl methacrylate (Merck), 2-hydroxyethyl methacrylate (Fluka). The polysiloxane was poly(methylhydrosiloxane), $n = 35$ (Merck).

Synthesis. 6-(*N*-Allylamino)-12-phenoxy-5,11-naphthacenequinone (III).[4] A solution of 6,11-diphenoxy-5,12-naphthacenequinone (0.5 g, 0.0011 mol)[4,5] in 500 mL of toluene was exposed to UV light overnight in a round-bottom Pyrex flask. A large excess of allylamine was added. The solution turned red immediately. According to TLC in toluene the reaction was complete immediately. The reaction mixture was filtered through a layer of silica gel. Traces of unreacted material were eluted with toluene. The red band was desorbed with methylene chloride from which a red solid was crystallized, mp 156-157 °C, yield 0.37 g (82%). ^{1}H NMR ($CDCl_3$): δ 1.57 (bs, 1 H, NH), 4.7 (1 peak, 2 H), 5.5-5.7 (m, 2 H), 5.9-6.4 (m, 1 H), 6.86-8.68 (aromatic ring, 13 H).

6-(*N*-(((Ethenylcarbonyl)oxy)propyl)amino)-12-phenoxy-5,11-naphthacenequinone (IV).[4] A solution of 6,11-diphenoxy-5,12-naphthacenequinone (0.5 g, 0.0011 mol)[4,5] in 500 mL of toluene was exposed to UV light overnight in a Pyrex flask. Aminopropanol (5 mL, i.e. a large excess) was added. After 10 min the reaction was complete. The reaction mixture was filtered through a column of silica using toluene as eluent. When no

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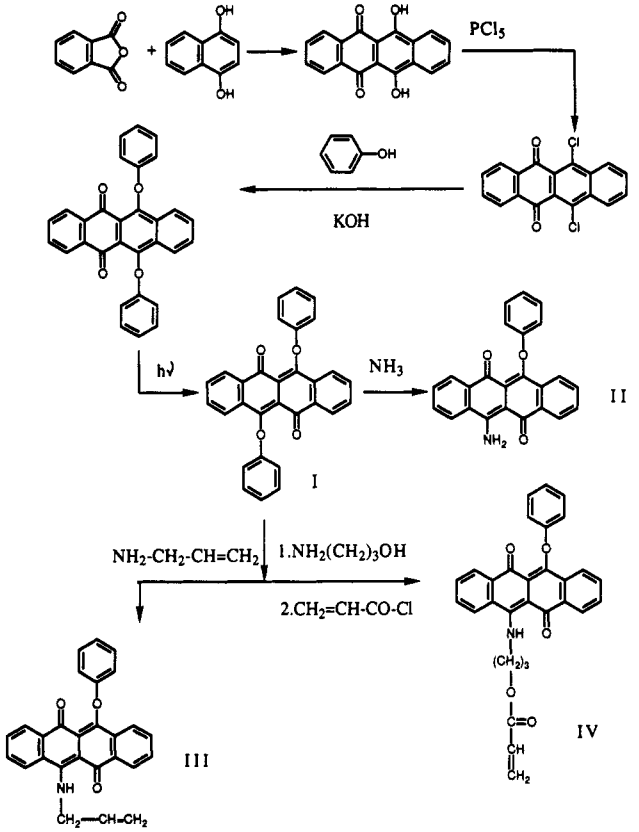
Scheme II
Synthesis of Photochromes and Photochrome Monomers (Type A)



further trace of the starting material was found in the eluent, it was changed to acetone. The solvent was evaporated to give red crystals of 6-(*N*-(hydroxypropyl)amino)-12-phenoxy-5,11-naphthacenequinone, which were dried and used as such in the next step.

To a cold solution of this compound (100 mg, 0.24 mmol) and of triethylamine (23.8 mL, 0.24 mmol) in tetrahydrofuran (THF, 20 ml) was added dropwise acryloylchloride (93.6 mL, 96 mmol). After the addition was complete, the temperature was allowed to reach room temperature and the reaction mixture stirred overnight. The tetrahydrofuran was evaporated and ethyl acetate added. The solution was washed with water several times, dried, and evaporated. Filtration through a silica cork and evaporation to dryness gave a clean product. Yield: 22%. ^{1}H NMR ($CDCl_3$): δ 2.3 (m, 2 H), 4.2 (t, 2 H), 4.4 (t, 2 H), 5.6–5.9 (m, 2 H), 6.1–6.35 (m, 1 H), 6.7–8.3 (aromatic ring, 13 H).

2-((1-Hydroxy-2-naphthyl)carbonyl)benzoic Acid (VII).[6] Naphthol (10.8 g, 0.07 mol), phthalic anhydride (16.8 g 0.11 mol), and boric oxide (7.8 g, 0.11 mol) were thoroughly mixed and heated at 180 °C for 1.5 h. The mass was extracted with boiling water and the residue dissolved in a sodium carbonate solution, filtered, and acidified. The precipitate was dissolved in acetone, dried, and evaporated. This material was used without further purification in the next step. Yield: 31 g (96%).

6-Chloro-5,12-naphthacenequinone (VIII).[4] Acid VII (0.5 g, 0.017 mol) and 2.14 g (0.01 mol) of phosphorus pentachloride were thoroughly ground, and the mixture was heated at 160–170 °C for 1 h. To the cooled reaction mass we added 3 mL of glacial acetic acid in small portions. The precipitate was filtered off, washed with acetic acid, and dried at room temperature. It was then hydrolyzed in 3 mL of sulfuric acid at 60 °C for 1 h and poured onto ice. The precipitate was filtered off, dried, and recrystallized from xylene. Yield: 0.3 g (60%). Mp: 258 °C. MS: m/e = 294, 292 (P). IR, ν_{max} (Nujol): 1680, 1270, 860, 798, 770, 750, 713 cm^{-1}.

4-(*N*-(*tert*-Butyloxycarbonyl)amino)phenol (BOC Aminophenol) (X).[7] A solution of di-*tert*-butyl dicarbonate (5 g, 0.023 mol) in dry THF was added dropwise to a cold solution (ice bath) of aminophenol (2.5 g, 0.023 mol) and triethylamine (3.3 mL, 0.023 mol) in dry THF. After the addition, the mixture was left to stir at room temperature overnight. The THF was then evaporated, and the oily residue was dissolved in 50 mL of ethyl acetate. The solution was shaken with 5% potassium sulfate and then with water, dried, and filtered, and the solvent was evaporated to give a white solid, which was crystallized from an ether/hexane mixture. Yield: 3.6 g (76%). Mp: 139–140 °C. ^{1}H NMR ($CDCl_3$): δ 1.5 (s, 9 H), 5.22 (ls, 1 H, NH), 6.05 (bs, 1 H, OH), 6.12 (d, 2 H), 7.16 (d, 2 H).

Tyrosine Methyl Ester (XII).[8] Dry HCl gas was introduced into a suspension of L-tyrosine (1.8 g, 0.01 mol) in absolute methanol (13 mL) until a clear solution was obtained. More absolute methanol (25 mL) was added and the reaction mixture boiled under reflux for about 6 h. The solution was cooled to room temperature and evaporated to dryness in vacuum.

The residue was dissolved in absolute methanol and reevaporated. The hydrochloride was dissolved in 10 mL of water, cooled in an ice bath, and neutralized with about 10 mL of 5 N NaOH. The ester crystallized and was collected on a filter, washed with cold water, and dried over P_2O_5. The material was recrystallized from ethyl acetate and used in the next step without further treatment.

***N*-(*tert*-Butyloxycarbonyl)tyrosine Methyl Ester (XIV).** This was synthesized as described for X. Yield: 76%. Mp: 100–101 °C. ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 9 H), 2.98 (d, 2 H), 3.7 (s, 3 H), 4.45 (m, 1 H), 4.95 (m, 1 H, NH), 6.75 (d, 2 H), 6.96 (d, 2 H).

***N*-(*tert*-Butyloxycarbonyl)tyrosine Butyl Ester (XV).** This was synthesized as described for tyrosine methyl ester (XII). Yield: 79%. Mp: 89–90 °C. ^{1}H NMR ($CDCl_3$): δ 0.91–1.84 (m, 7 H), 1.41 (s, 9 H), 3.02 (d, 2 H), 4.1 (t, 2 H), 4.5 (m, 1 H), 5.0 (m, 1 H), 6.72 (d, 2 H), 7.0 (d, 2 H). MS: m/e (relative intensity) = 338 (6.26, P + H), 282 (4.47, P – C_4H_8), 238 (5.48, P – $C_5H_8O_2$).

6-[(*N*-(*tert*-Butyloxycarbonyl)tyrosine methyl ester)-*O*-yl]-5,12-naphthacenequinone (XVIII). A mixture of chloronaphthacenequinone (VIII) (2 g, 0.007 mol), *N*-(*tert*-butyloxycarbonyl)tyrosine methyl ester (XIV) (3 g, 0.01 mol), and potassium carbonate (1.2 g, 0.009 mol) in dry DMF (20 mL) was heated to 110 °C for 3 h. It was then poured over slightly acid ice water. The precipitate was filtered, rinsed with cool water several times, and dried. The product was flash chromatographed using silica as sorbent and toluene as a first eluent, followed by a 1:4 mixture of ethyl acetate and hexane. Yield: 1.9 g (50%). ^{1}H NMR ($CDCl_3$): δ 1.41 (s, 9 H), 2.99 (d, 2 H), 3.72 (s, 3 H), 4.47 (m, 1 H), 5.0 (d, 1 H), 6.76 (d, 2 H), 7.64–8.8 (aromatic rings, 9 H).

6-((Tyrosine methyl ester)-*O*-yl)-5,12-naphthacenequinone (XX). 6-[(*N*-(*tert*-Butyloxycarbonyl)tyrosine methyl ester)-*O*-yl]-5,12-naphthacenequinone (XVIII) (1 g, 0.0018 mol) was dissolved in TFA and left to stir at room temperature for 1 h. Most of the TFA was then removed by flushing with argon gas. The residue was neutralized with $NaHCO_3$ to pH 9. The product was extracted with ether to give a red solid. Yield: 0.49 g (60%). The amine tended to oxidize quickly and was therefore used immediately without any further treatment.

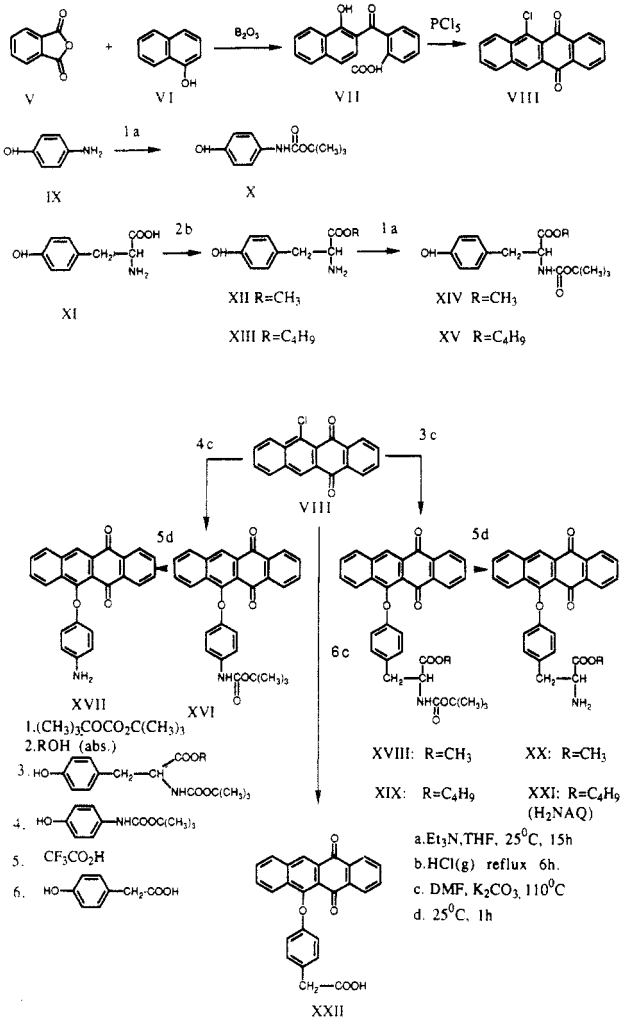
6-[((*tert*-Butyloxycarbonyl)tyrosine butyl ester)-*O*-yl]-5,12-naphthacenequinone (XIX). This was obtained as described for compound XVIII. Yield: 75%. Mp: 167–170 °C. ^{1}H NMR ($CDCl_3$): δ 0.89 (t, 3 H), 1.25–1.37 (m, 4 H), 1.4 (s, 9 H), (broad peak, 2 H), 4.07 (t, 2 H), 4.5 (m, 1 H), 4.98 (d, 1 H), 6.8 (d, 2 H), 7.04 (d, 2 H), 7.65–8.8 (aromatic rings, 9 H). CIMS: m/e 593 (M^-).

6-((Tyrosine butyl ester)-*O*-yl)-5,12-naphthacenequinone (XXI). This was obtained as described for product XX and used without further purification. Yield: 74%.

6-[(4-(Carboxymethyl)phenyl)oxy]-5,12-naphthacenequinone (XXII). This was obtained as described for product XVIII. The product was flash-chromatographed through silica, the eluents were methylenchloride and then THF. Yield, 44%. Mp: 220–224 °C (decomposition). ^{1}H NMR (DMSO): δ 3.27 (s, 2 H); 6.69 (d, 2 H); 7.14 (d, 2 H); 7.81 (m, 4 H); 8.15 (m, 4 H); 8.25 (s, 1 H). CIMS: m/e 409 (MH^+), 408 (M^-).

6-[(4-(*N*-(*tert*-Butyloxycarbonyl)amino)phenyl)oxy]-5,12-naphthacenequinone (XVI). The product was obtained as described for compound XVIII. The solid material was tirturated with methanol to give a yellow material. Yield 29%.

Scheme III
Synthesis of Photochromes (Type B)



Mp: 234–236 °C. ^{1}H NMR (DMSO): δ 1.44 (s, 9 H); 6.78 (d, 2 H); 7.3 (d, 2 H); 7.74-8.34 (m, 8 H); 8.86 (s, 1H).

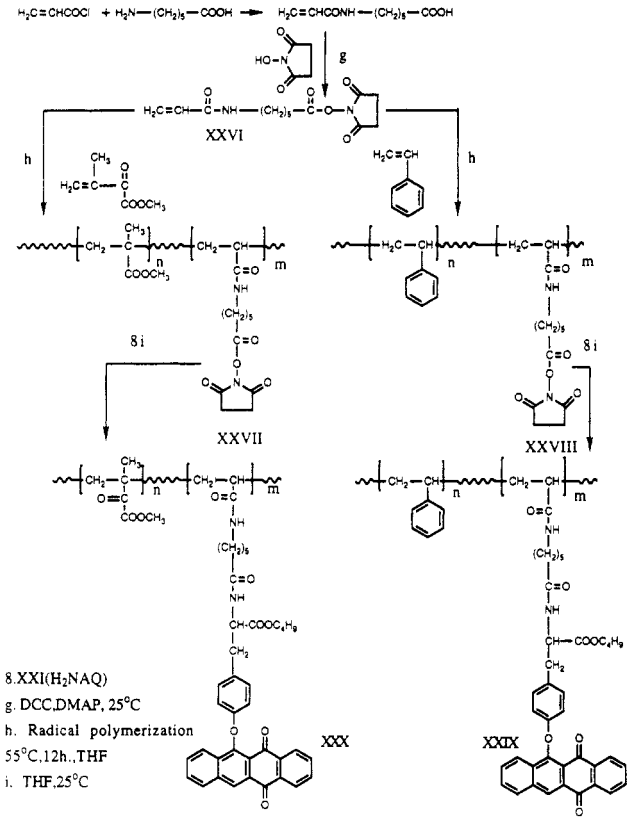
6-[(4-Aminophenyl)oxy]-5,12-naphthacenequinone (XVII). The product was obtained as described for product XX (yield 70%). Since it is not stable, it was used quickly without further treatment. MS: *m/e* (relative intensity) = 274 (30.65, P – C_6H_5N), 246 (1.95, P – C_7H_5NO), 218 (3.74, P – $C_8H_5NO_2$), 189 (33.56, P – $C_9H_6NO_3$), 163 (5.72), 109 (100, C_6H_7NO), 95 (20.42).

Synthesis of the Photochromic Polymers. The syntheses of acrylate and styrene polymers are described in Scheme IV. The monomer XXVI was synthesized as described.[9,10] The polymers XXVII and XXVIII were synthesized by free radical copolymerization of monomer XXVI with styrene or with methyl methacrylate in THF as described.[11] NH_2AQ, XXI, was incorporated in the copolymers by the reaction of the active ester copolymers XXVII and XXVIII with amine XXI.[12] Copolymers XXIX and XXX were precipitated (MMA copolymer by ether, styrene copolymer by methanol), purified by reprecipitation, and freeze-dried from benzene. The yield of the polymers was about 25%.

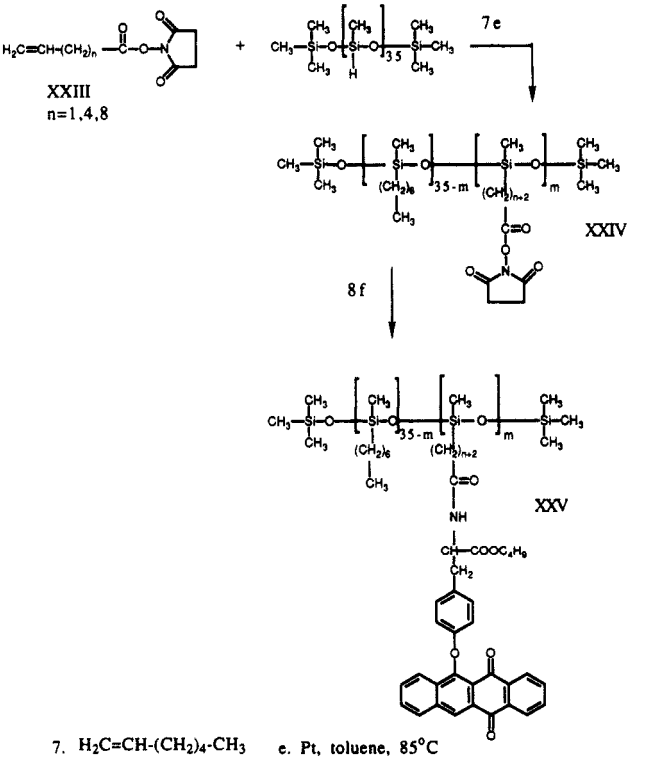
The composition of the polymers was determined by spectroscopic measurements.[11]

The preparation of polysiloxane polymers containing photochrome is given in Scheme V. XXIII was synthesized as described.[12] Polysiloxanes XXV were synthesized by a polymer-analogous reaction in two steps. The active ester–heptene copolymers were prepared by addition of the olefines via a hydrosilylation reaction to Si–H-containing polymers as described.[9] The ratio between the active ester and the heptene varied in the range 1:9 to 1:1. This is expressed by the letter *m* in formulas XXIV and XXV. XXI was then incorporated in the copolymers by reaction of the active ester copolymers (XXIV) with the amine of XXI.[12] The copolymers XXV were isolated

Scheme IV
Synthesis of Acrylic and Styrene Polymers Containing Photochrome Type B



Scheme V
Synthesis of Polysiloxanes Containing Photochrome Type B



by repeated precipitation with methanol and freeze dried from benzene. The yield of the polymers was about 30%.

Characterization of Materials. ^{1}H NMR spectra were recorded in $CDCl_3$ or in DMSO on FT 80A Varian or AMX 400 Bruker spectrometers, using tetramethylsilane as an internal

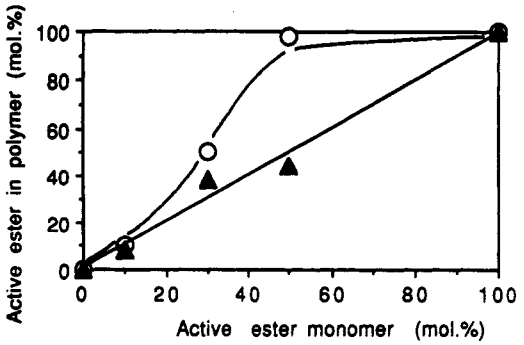


Figure 1. Content of active ester incorporated in the polymers as a function of the feed composition: (▲) methyl methacrylate copolymer; (○) styrene copolymer.

standard. The IR spectrum was recorded on a FTIR Nicolet 50 spectrometer. High-resolution mass spectra were measured on a Finnigan 4500 instrument, using direct inlet. Chemical ionization mass spectra were measured on a Finnigan TSQ-70 instrument, using isobutane gas as the ionizing agent. Negative and positive ionic monitoring were used. Melting points were determined on a Fisher-Johns melting point apparatus and given without correction. Optical absorption spectra were recorded on a Varian 2200 spectrophotometer.

Film Preparation. Films were prepared by dipping glass slides into a 20% polymer solution and slow evaporation of the solvent, followed by drying in vacuo. The film thickness was about 1 μm.

Results and Discussion

Since the photochromes described in the present paper contain the very reactive quinone group, the synthesis of polymers containing these photochromes presents a formidable synthetic problem.

Attempts to synthesize photochromic polysiloxane polymers by polymer-analogous reactions, in one step, using monomer III and heptene, failed.

Another attempt to synthesize photochromic acrylate polymer in one step by free radical copolymerization of monomer IV and methyl methacrylate failed too. These results can be attributed to the fact that the quinone moiety acted either as a catalyst poison or as a radical scavenger.

Another attempt to introduce a B-type photochrome into a polymer by direct esterification of acid XXII with a polymer containing hydroxy groups also failed. Anhydrides of the acid were obtained and no photochromic polymer was observed.

Amine XVII and amino methyl ester XX were not suitable because of their low solubility, but amino butyl ester XXI dissolves well in many organic solvents. Moreover, it has also excellent photochromic properties and was, therefore, used in the preparation of photochromic polymers, as described in Schemes IV and V.

The composition of acrylic and styrene copolymers as a function of the feed composition is plotted in Figure 1. This composition was monitored by NMR using the singlet peak of hydroxysuccinimide at 2.81. Results in Figure 1 indicate that the reactivity of monomer-active ester, step h in Scheme IV, is much bigger than the reactivity of styrene while methyl methacrylate shows similar reactivity. This difference can be attributed to steric hindrance in the case of styrene.

Figure 2 indicates that the molar content of photochrome in both polymers is similar to that of the active ester.

Polysiloxanes were checked in analogy to acrylate polymers. Figure 3 shows that the molar concentration of active ester in the polymer is higher than in the monomer feed, while Figure 4 indicates that the concentration of

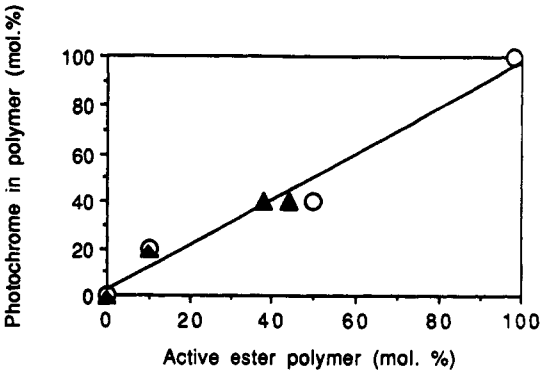


Figure 2. Content of photochrome incorporated in the copolymers as a function of the active ester in copolymers: (▲) methyl methacrylate copolymer; (○) styrene copolymer.

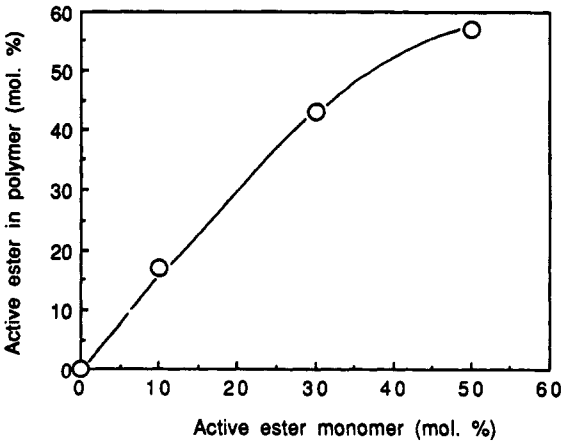


Figure 3. Content of active ester incorporated in the polysiloxane copolymer as a function of the feed composition.

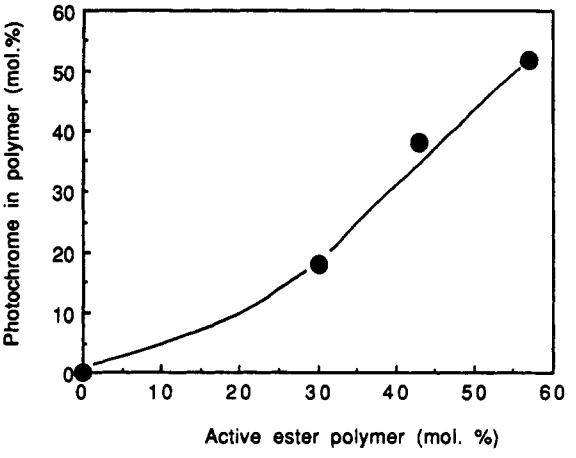


Figure 4. Content of photochrome incorporated in the polysiloxane copolymer as a function of the active ester in polysiloxane copolymer.

photochrome incorporated in the polymer is smaller than that of active ester polymer in the feed. Another interesting result is that using different spacers, $n = 1, 4, 8$, in XXIII, did not affect these results significantly.

Absorption Spectra and Kinetics of the Photoconversion "trans" → "ana". The spectra of the photochrome XXI and the photochromic polymers are shown in Figure 5, before and after UV irradiation. The *p*-quinone (=trans) form has its absorption peak at around 400 nm, while the ana form displays the typical double peaks at about 450 and 480 nm, as described for 5-phenoxy-6,12-naphthacenequinone.[1,2] It is evident that the photochemical conversion is decreasingly retarded by the polymer matrix as we go from styrene to methyl meth-

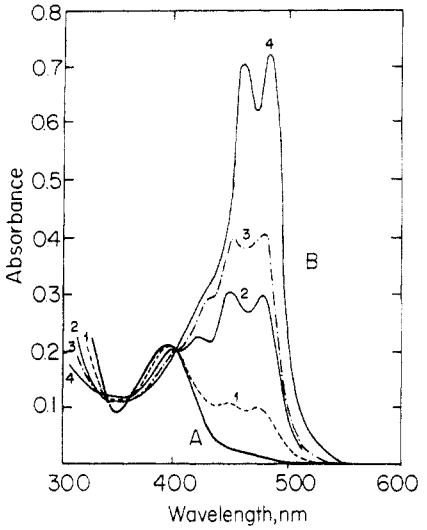


Figure 5. Absorption spectra before (A) and after (B) irradiation by light at 405 nm during 15 min: (1) film of the styrene photochromic copolymer; (2) film of the methyl methacrylate photochromic copolymer; (3) film of the polysiloxane photochromic copolymer; (4) solution of the pure photochrome XXI, 1.01×10^{-4} mol/L in 1 cm cell. Spectrum A before irradiation was roughly the same in samples 1–4.

acrylate to polysiloxane. The latter two thus seem to be the most promising ones for possible applications.

A detailed account of the reversible photochemistry of all three photochromic polymers, in comparison with the photochromes proper, will be published.

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