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POLYMERS WITH PENDANT CYANATE ESTER GROUPS: SYNTHESIS, THERMAL CURING AND PHOTOCROSSLINKING

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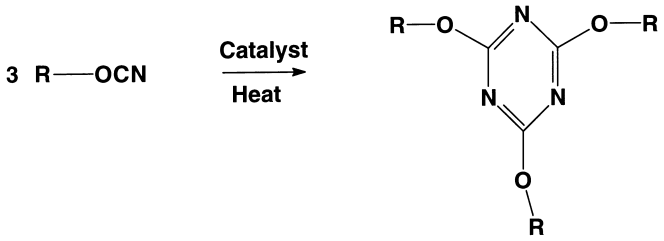
Abstract—The new monomers 4-vinylphenyl cyanate and 2,6-dimethyl-4-vinylphenyl cyanate were prepared from 4-hydroxyacetophenone and 3,5-dimethyl-4-hydroxyacetophenone as starting materials. The styrene copolymers of the cyanate ester monomers were prepared via free radical polymerization. The copolymers were sensitive to UV light and became crosslinked after irradiation with 254 nm light. The cyanate ester groups in the copolymer of 2,6-dimethyl-4-vinylphenyl cyanate isomerized to isocyanate groups during UV irradiation. Thermal curing of the copolymers with 4-nonylphenol as catalyst yielded networks containing cyanurate groups. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

During the past few years, the chemistry and technology of cyanate esters has found increased interest in the field of thermosetting resins. The thermal curing reaction is based upon the cyclotrimerization reaction of cyanic acid esters (R-OCN) which yields triazine derivatives [1] as depicted in Scheme 1. The trimerization occurs at elevated temperatures and is catalyzed by phenols, amines, Brønsted acids and metal complexes such as copper acetylacetonate [2].



Scheme 1

In the case of di- and polyfunctional cyanates, crosslinked polymers are produced upon thermal curing. These materials, commonly designated as cyanate ester resins, show low density, little moisture uptake and low dielectric constants [3]. These properties make them the materials of choice for applications in the fields of electronics and aerospace industries. In spite of their high price the demand for cyanate ester resins has grown continuously since their introduction around 1980.

For the build-up of cyanate ester resins, bifunctional aromatic compounds, e.g. derivatives of bis(phenol) A, are almost exclusively applied [4]. Aliphatic cyanate esters are in general thermally unstable and isomerize to the corresponding isocyanates during storage [5, 6]. However, perfluorinated aliphatic cyanate esters have sufficient stability [7] and resins made therefrom have promising properties for commercial applications [8].

Multifunctional cyanate esters are also of technical interest [4]. Cyanated low-molecular-weight adducts of phenol and dicyclopentadiene are commercially available. In a similar way cyanated phenol–formaldehyde oligomers are used as thermostets with exceptionally high glass transition temperatures T_g. However, until today no well-defined polymer containing a cyanate ester group in

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the repeating unit has been described. Vinyl monomers bearing OCN groups groups have also not been reported. As an exception 2,6-di-*tert*-butyl-3-vinylphenyl cyanate has been claimed in a patent, but nothing has been reported about polymers from this monomer [9].

Generally, the photochemistry of cyanate esters has not found much attention either. Hara *et al.* [10] investigated the photolysis of *n*-butyl cyanate, and found *n*-butyl isocyanate and *n*-butyl isocyanurate as the main reaction products. A study on the photoreactions of aromatic cyanate esters showed that both a fission in phenoxy and cyano radicals as well as an isomerization to the corresponding isocyanates occurs [11]. The mechanism of the photoisomerization was not clarified and remained under discussion [12].

Only recently photosensitive cyanate ester resins have been reported in the patent literature [13–15]. In the formulations described, Brønsted acids [13] or organometallic compounds [14, 15], which act as trimerization catalysts, are generated by photochemical reactions. However, possible photoreactions of the cyanate ester monomers themselves have not been taken into consideration.

The aim of the present investigation is the synthesis and polymerization of the monomers 4-vinylphenyl cyanate (**4a**) and 2,6-dimethyl-4-vinylphenyl cyanate (**4b**). The styrene copolymers (**5a**, **5b**) of these monomers were characterized and the feasibility of the thermal and UV curing was investigated. The photolysis of phenyl cyanate (**6**) and 2 6-dimethylphenyl cyanate (**7**) as low-molecular-weight model compounds was studied.

EXPERIMENTAL

Measurements

The weight-average molecular weight $\bar{M}_W$ and the polydispersity index *PDI* were determined by size exclusion chromatography (GPC) with polystyrene gel columns (10^3, 10^4 and 10^6 Å, size 5 μm, tetrahydrofuran as eluent) using a Viscotec Model 200 differential refractometer/viscometer as the detector (universal calibration).

Infrared (IR) spectra were recorded with a Bomem M 100 Fourier transform IR spectrometer. Ultraviolet (UV) spectra were taken with a Hewlett-Packard HP 8452 A spectrometer. ^{1}H nuclear magnetic resonance (NMR) spectrometer measurements were carried out with a Bruker WH90 spectrometer (90 MHz).

Gas chromatography (GC)/mass spectrometry (MS) coupling was performed with a combination of a Shimadzu GC-14A gas chromatograph (HP-1 column) and a Kratos Profile double-focusing mass spectrometer (EI ionization at 70 eV).

Synthesis of 4-(1-hydroxyethyl)phenol **(2a)**

4-Hydroxyacetophenone (**1a**) was reduced to a 4-(1-hydroxyethyl) phenol (**2a**) with a Cu–Ba–Cr oxide catalyst. The catalyst was prepared according to a literature method [16] and activated before use. The activation was carried out in an autoclave at 110°C and 120 bar hydrogen pressure for 120 min. 20 g (0.147 mol) of the ketone (**1a**) were dissolved in 150 mL of ethanol and mixed with 4 g of the activated catalyst. The reaction slurry was autoclaved at 90°C and 100 bar hydrogen pressure under stirring. After 8 hours reaction time, the catalyst was filtered off and the remaining solution was concentrated *in vacuo* to give 19.6 g (0.142 mol) of crude 4-(1-hydroxyethyl)phenol (**2a**), yield 95.3%. An analytical sample was purified by silica column chromatography with cyclohexane/ethyl acetate (vol. ratio 10:8) as eluent. m.p. 129–130°C. IR (KBr pellet): 3318 (—OH), 1614, 1514, 1451, 1236, 1074, 1006, 897, 832 cm^{-1}. ^{1}H-NMR (acetone-d_6): δ = 1.30 (d, —CH_3, 3H), 4.75 (q, —CH, 1H), 6.70–7.20 (aromatic, 4H).

Synthesis of 4-(1-hydroxyethyl)phenyl cyanate **(3a)**

19.5 g (0.141 mol) of the crude phenol (**2a**) were dissolved in 100 ml of acetone. The solution was cooled to −30°C and 8.70 g (0.141 mol) of liquefied cyanogen chloride were added under stirring. Within a period of 60 min a solution of 14.3 g (0.141 mol) of triethyl amine in 50 mL of acetone was added dropwise. During the addition the temperature of the reaction solution was maintained between −30°C and −20°C. The solution was then stirred for further 60 min at room temperature to complete the reaction. These operations were carried out under appropriate safety precautions in a well-ventilated hood. After filtration the reaction solution was concentrated *in vacuo*. The oily residue was chromatographed over a silica gel column using cyclohexane/ethyl acetate (vol. ratio 10:3) as eluent. 8.5 g (52 mmol) of the cyanate (**3a**) were obtained as an oily liquid, yield 36, 9%. IR (film on NaCl disc): 3399 (—OH), 2974, 2277 (—OCN), 2239 (—OCN), 1602, 1501, 1205, 1167, 1086, 1012, 900, 835 cm^{-1}. ^{1}H-NMR (acetone-d_6: δ = 1.40 (d, —CH_3, 3H), 4.90 (q, —CH, 1H), 7.15–7.45 (aromatic, 4H).

Synthesis of 4-vinylphenyl cyanate **(4a)**

A three-necked 50 mL flask was equipped with a distillation head, a dropping funnel and a capillary as nitrogen inlet. 2.0 g (14.7 mmol) of fused $KHSO_4$ were finely ground and placed in the flask. After loading the dropping funnel with 5.7 g (35 mmol) of the cyanate (**3a**), the distillation apparatus was evacuated to 2 torr and heated in an oil bath thermostatted at 240°C. The contents of the dropping funnel were dropped into the heated flask over a period of 30 min. 1.6 g of a crude distillate were obtained containing large amounts of the unreacted cyanate (**3a**). After chromatography over silica gel with cyclohexane/ethyl acetate (vol. ratio 10:2) as eluent, 0.28 g (1.93 mmol) of 4-vinylphenyl cyanate (**4a**) were obtained, yield 5.5%. IR (film on NaCl disc): 2268 (—OCN), 2236 (—OCN), 1632 (C═C), 1597, 1500, 1209, 1188, 1167, 836 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 5.30 (d, ═CH_2, 1H), 5.70 (d, ═CH_2, 1H), 6.70 (d of d, —CH═, 1H), 7.20–7.50 (aromatic, 4H).

Synthesis of 2,6-dimethyl-4-(1-hydroxyethyl)phenol **(2b)**

3,5-Dimethyl-4-hydroxyacetophenone (**1b**) was prepared according to Benington *et al.* [17]. 18.0 g (0.11 mol) of compound (**1b**) were dissolved in 150 ml of ethanol. To this solution, 15.0 g (0.40 mol) of $NaBH_4$ were added in small portions over a period of 30 min. After the addition was complete, stirring was continued for 5 hours at room temperature. The reaction solution was then poured into 500 mL of ice-cold water and acidified with concentrated HCl to pH 3. The aqueous phase was saturated with NaCl and extracted with methylene chloride (three times with 150 ml each). The extract was concentrated *in vacuo* and chromatographed over silica gel using cyclohexane/ethyl acetate (vol. ratio 10:2) as eluent. 10.5 g (63 mmol) of the phenol (**2b**) were obtained, yield 57%. m.p. 109–110°C. IR (KBr pellet): 3399 (—OH), 2974, 2927, 1606, 1487, 1208, 1151, 1095, 1031, 945, 876 cm^{-1}. ^{1}H-NMR ($CDCl_3$):

δ = 1.40 (d, —CH_3, 3H), 2.25 (s, —CH_3, 6H), 4.80 (q, —CH, 1H), 6.9 (s, aromatic, 2H).

Synthesis of 2,6-dimethyl-4-(1-hydroxyethyl)phenyl cyanate (**3b**)

10.0 g (60 mmol) of the phenol (**2b**) were treated with cyanogen chloride as described for compound (**3a**). The crude product was chromatographed over silica gel with cyclohexane/ethyl acetate (vol. ratio 10:3) as eluent. 6.9 g (36 mmol) of the cyanate (**3b**) were obtained as a yellowish oil, yield 60%. IR (film on NaCl disc): 3384 (—OH), 2974, 2925, 2259 (—OCN), 1478, 1139, 946, 876 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 1.40 (d, —CH_3, 3H), 2.35 (s, —CH_3, 6H), 4.80 (q, —CH, 1H), 7.10 (s, aromatic, 2H).

Synthesis of 2,6-dimethyl-4-vinylphenyl cyanate (**4b**)

4.70 g (25 mmol) of the cyanate (**3b**) were dehydrated in the manner described for compound (**4a**). The crude distillation product (1.9 g) was purified by twofold silica gel chromatography using cyclohexane/ethyl acetate (vol. ratio 12:1) as eluent. 0.29 g (1.68 mmol) of the cyanate (**4b**) were obtained as a colorless liquid, yield 6.7%. IR (film on NaCl disc): 2924, 2272 (—OCN), 2250 (—OCN), 1633 (C═C), 1597, 1479, 1182, 1138, 990, 914, 878 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ = 2.35 (s, —CH_3, 6H), 5.30 (d, ═CH_2, 1H), 5.70 (d, ═CH_2, 1H), 6.65 (d of d, ═CH—, 1H), 7.10 (s, aromatic, 2H).

Copolymerization of 4-vinylphenyl cyanate (**4a**) with styrene to give copolymer (**5a**)

210 mg (1.45 mmol) of 4-vinylphenyl cyanate (**4a**), 603 mg (5.79 mmol) of styrene and 11.9 mg (0.07 mmol) of AIBN were dissolved in 2.7 mL of toluene. The reaction vessel was degassed by three freeze–thaw–freeze cycles, sealed under nitrogen and immersed in a water-bath thermostatted at 65°C. During the reaction time (7 hours), light was excluded. The polymerization was terminated by cooling of the vessel, then the reaction solution was diluted with 5.0 mL of toluene and precipitated in a tenfold excess of pentane. The polymer was purified by twofold reprecipitation from methylene chloride/pentane and finally dried *in vacuo* to constant weight. The yield was 240 mg; this corresponds to 29.5% conversion.

Copolymerization of 2,6-dimethyl-4-vinylphenyl cyanate (**4b**) with styrene to give copolymer (**5b**)

200 mg (1.16 mmol) of the monomer (**4b**), 480 mg (4.62 mmol) of styrene and 9.5 mg (0.06 mmol) of AIBN were dissolved in 2.9 mL of toluene. The polymerization (10 hours at 65°C) and workup of the reaction solution was carried out in the way described for the copolymer (**5a**). The yield was 250 mg (37% conversion).

Synthesis of phenyl cyanate (**6**) and 2,6-dimethylphenyl cyanate (**7**)

Phenyl cyanate (**6**) and 2,6-dimethylphenyl cyanate (**7**) were prepared from the corresponding phenols following a literature method [18]. The compounds were distilled *in vacuo* and then chromatographed over a silica column using cyclohexane/ethyl acetate (vol. ratio 10:1) as eluent.

Thermal curing experiments

Films of the copolymers (**5a**) and (**5b**) containing 5 weight-% of 4-nonylphenol were cast on NaCl plates and dried *in vacuo*. The liquid cyanates (**6**) and (**7**) were placed between CaF_2 plates using a 0.1 mm teflon foil as spacer. The test specimens were thermostatted in a heatable infrared cell (Specac Model 5750) under a nitrogen atmosphere. At intervals, absorbance IR spectra were recorded to follow the curing process. Conversion of the cyanate ester groups was calculated from the integrated IR bands between 2120 and 2380 cm^{-1} (—OCN).

Irradiation of phenyl cyanate (**6**) and 2,6-dimethylphenyl cyanate (**7**) in solution

Solutions of the cyanates (**6**) and (**7**) in cyclohexane (3 weight-%) were irradiated with the unfiltered light of a mercury lamp (Heraeus type Q 1023). A stream of nitrogen was passed through the solutions being irradiated. After 60 min of irradiation, the samples were immediately subjected to GC/MS analysis.

Photocrosslinking of the copolymers (**5a**) and (**5b**)

The copolymers were cast on CaF_2 or quartz plates with a Suss RC5 Standard spin coater from chloroform solutions. After drying *in vacuo* for three hours at 20°C, the samples were irradiated under nitrogen. A mercury lamp (Heraeus type Q 1023) equipped with a 254 nm interference filter (Melles Griot) was used as the light source. The light intensity at the sample surface was 30.1 $mJ \cdot cm^{-2} \cdot min^{-1}$ as determined by ferrioxalate actinometry [19].

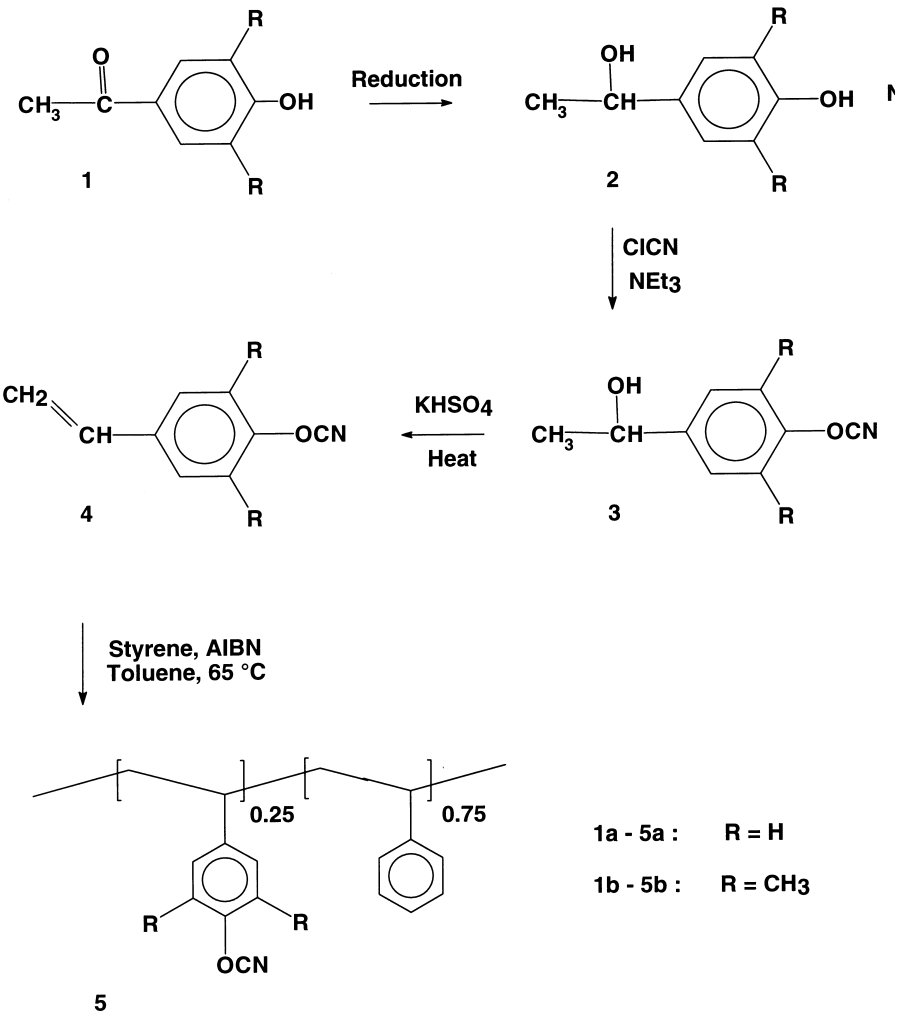
After irradiation the sample plates were immersed in methylene chloride (15 min, 20°C), rinsed with methylene chloride and then dried *in vacuo*. The insoluble fraction W of the copolymers was determined from the change in film thickness before and after development. The change in film thickness was calculated from the UV absorbance at 262 nm. The absolute film thickness r was estimated from interferometric measurements before the irradiation experiments. The films of copolymer (**5a**) had a thickness of 1.0 μm, in the case of copolymer (**5b**) the thickness was 0.5 μm.

RESULTS AND DISCUSSION

Preparation of the monomers (**4a**) and (**4b**) and of the copolymers (**5a**) and (**5b**)

For the preparation of polystyrenes ring-substituted with cyanate (OCN) groups, various synthetic pathways can be considered. The most common way to prepare aromatic esters of cyanic acid is the reaction of phenols with cyanogen halides such as ClCN or BrCN in the presence of triethyl amine. Copolymers of vinylphenols with styrene are available and a polymer analogous reaction which transforms the phenol groups into cyanate groups should be possible. However, side reactions lead to the formation of imidocarbonates and cannot be excluded during synthesis. In order to obtain well-defined polymers it is generally advantageous to carry out copolymerization reactions with monomers bearing the desired functionalities. We therefore searched for a way to prepare monomers bearing both a vinyl and an OCN group as substituents.

Monomeric vinylphenols are generally unstable [20] and thus unsuitable as starting compounds for a cyanation reaction. We decided to introduce the OCN group first and then—in a subsequent step—to generate the vinyl substituent by a dehydration reaction. The reaction sequence for the monomers 4-vinylphenyl cyanate (**4a**) and 2,6-dimethyl-4-vinylphenyl cyanate (**4b**) is shown in Scheme 2.



Scheme 2

Although the carbinols (**2a**) and (**2b**) have been reported in the literature [21, 22], a convenient method for their preparation is given in the experimental section. The intermediates (**3a**) and (**3b**) as well as the monomers (**4a**) and (**4b**) have as yet not been described.

In the first step of the reaction sequence, the acetophenones (**1a**) and (**2a**) are reduced to the corresponding carbinols (**2a**) and (**2b**). It is noteworthy that the reduction of compound (**1a**) can be carried out with hydrogen employing a Cu–Ba–Cr oxide catalyst, but not with $NaBH_4$ in ethanolic solution. On the other hand, compound (**1b**) was readily reduced by $NaBH_4$ but remained unchanged in the presence of hydrogen and the Cu–Ba–Cr oxide catalyst.

Transformation of the carbinols (**2a**) and (**2b**) into the cyanates (**3a**) and (**3b**) was achieved with cyanogen chloride (ClCN) and triethylamine in fair yields (37 and 60%, respectively). It was advantageous to carry out the chromatographic purification immediately after the synthesis. The crude cyanates (**3a**) and (**3b**) decomposed within 24 hours of standing, whereas the purified compounds could be stored for several days.

Dehydration of the cyanates (**3a**) and (**3b**) to the desired vinyl monomers (**4a**) and (**4b**) was achieved by the method of Saunders and Overberger [23] using $KHSO_4$ as the dehydration catalyst. The low yields of this reaction step (5.5 and 6.7%, respectively) may be explained by the sensitivity of aromatic cyanates towards Brønsted acids, which initiate the trimerization to give cyanurates.

Once obtained in a pure form, the monomers (**4a**) and (**4b**) are stable compounds which can be stored for one week (temperature 4°C, exclusion of light) without any noticeable change in their properties.

Synthesis and characterization of the copolymers (**5a**) and (**5b**)

The free radical homopolymerization of 4-vinylphenyl cyanate (**4a**) in dimethylformamide (DMF) yielded a polymer which became insoluble upon drying. The styrene copolymers (**5a**) and (**5b**) con-

Table 1. Characterization of the copolymers (**5a**) and (**5b**)

Copolymer	(**5a**)	(**5b**)
Molar fraction of cyanate ester monomers in the copolymers	0.25	0.25
$\bar{M}_W$ (in g·mol^{-1})	35200	29100
PDI ($\bar{M}_W/\bar{M}_n$)	1.67	1.55
E_g (in mJ·cm^{-2})	40	220

taining 25 mol% of the comonomers (**4a**) and (**4b**), respectively, remained fully soluble even after four weeks of storage (4°C, exclusion of light). The IR spectra of the copolymers (**5a**) and (**5b**) showed a split band around 2258 cm^{-1} which is characteristic of the cyanate group. Bands typical of phenols and isocyanates were completely absent. This indicated that the free radical polymerization at 65°C left the OCN groups unaffected and that the copolymers had structures as shown in Scheme 2.

The characteristic data of the copolymers (**5a**) and (**5b**) (composition, average molecular weight $\bar{M}_W$, polydispersity index *PDI* and gel dose E_g) are summarized in Table 1.

Thermal curing of the copolymers (**5a**) and (**5b**)

We were interested to know whether cyanate groups covalently bound to a polymer backbone undergo a cyclotrimerization reaction as is well-known for low-molecular-weight cyanates [1]. 4-Nonylphenol as curing catalyst [2] was added to the copolymers (**5a**) and (**5b**) at a concentration of 5 weight-%, then the samples were cured at a temperature of 180°C.

Figure 1 shows the IR spectra of copolymer (**5a**) before and after thermal treatment (25 hours at 180°C). The bands at 1564 cm^{-1} (triazine ring vibration), 1367 and 1212 cm^{-1}, which appeared after thermal treatment, prove the formation of a cyanurate network. This can be deduced from the IR spectrum of 2,4,6-triphenoxy-*s*-triazine [24] which displays signals at 1563, 1370 and 1205 cm^{-1}. A similar result was found for copolymer (**5b**), which displayed new IR bands at 1558, 1364 and 1189 cm^{-1} after curing.

The conversion of the cyanate ester groups as a function of the curing time is plotted in Fig. 2. In the case of copolymer (**5a**) the trimerization reaction was almost complete after 34 hours (ca. 97% conversion). With copolymer (**5b**) a conversion of 75% was obtained after 38 hours. The intersection of the curves in Fig. 2 might be a result of the complex reaction sequence of cyclotrimerization [1].

For comparison we carried out curing experiments with phenyl cyanate (**6**) and 2,6-dimethylphenyl cyanate (**7**) as low-molecular-weight model compounds. These experiments were carried out under the same conditions as for the copolymers (**5a**) and (**5b**). With 5 weight-% of 4-nonylphenol as catalyst, the trimerization reaction was completed after 60 min (phenyl cyanate, **6**) and after 90 min (2,6-dimethylphenyl cyanate, **7**). The comparison shows that the curing speed of the copolymers (**5a**) and (**5b**) is low compared to low-molecular-weight cyanate esters, which can be readily explained by the reduced mobility of the polymer-bound OCN groups.

Photoreactions of phenyl cyanate (**6**) and 2,6-dimethylphenyl cyanate (**7**) in solution

The irradiated cyclohexane solution of phenyl cyanate (**6**) contained only small amounts of new products and a large fraction of the cyanate (**7**) remained unchanged. The main photolysis products

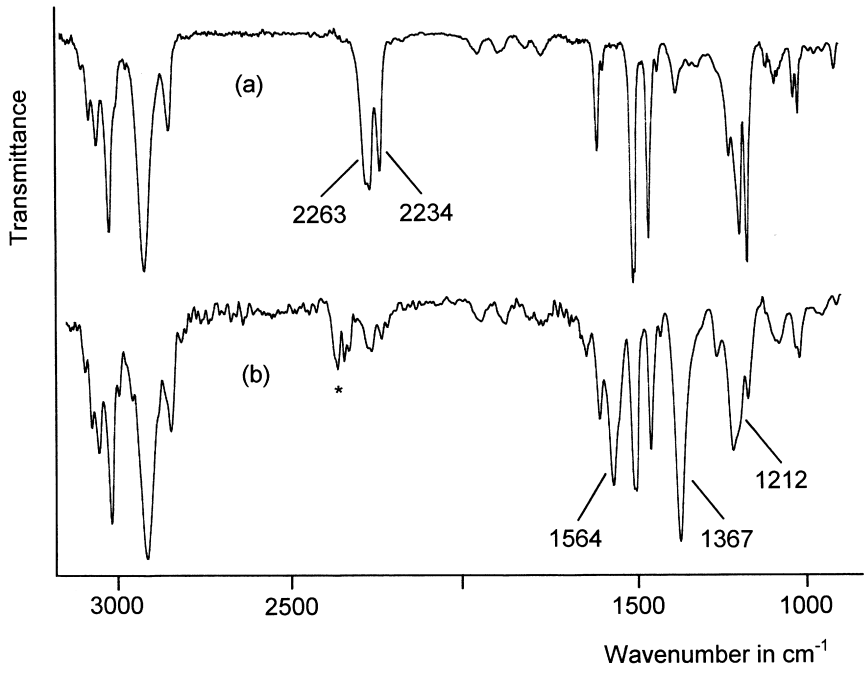


Fig. 1. IR spectra of copolymer (**5a**): (a) before; (b) after thermal curing (25 hours at 180°C; 4-nonylphenol as catalyst). The IR band marked with * originates from CO_2.

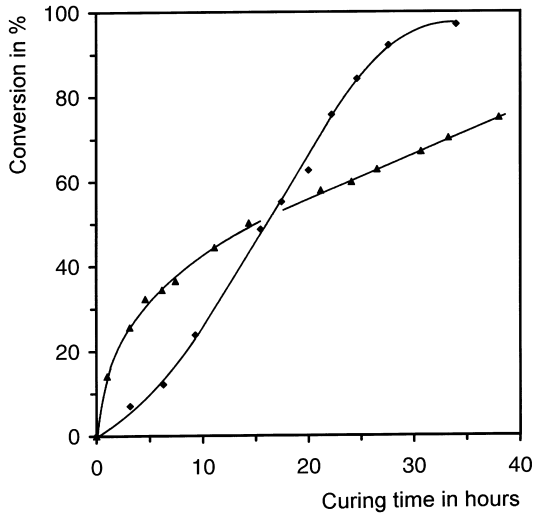


Fig. 2. Conversion of the OCN groups in the copolymers (**5a**) and (**5b**) as a function of time (180°C; 4-nonylphenol as catalyst): ◆, copolymer (**5a**); ▲, copolymer (**5b**).

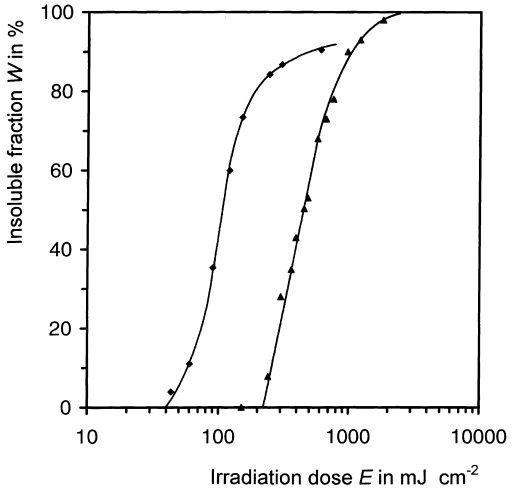


Fig. 3. Photocrosslinking of the copolymers (**5a**) and (**5b**) (254 nm). Insoluble fraction W as a function of irradiation dose E: ◆, copolymer (**5a**); ▲, copolymer (**5b**).

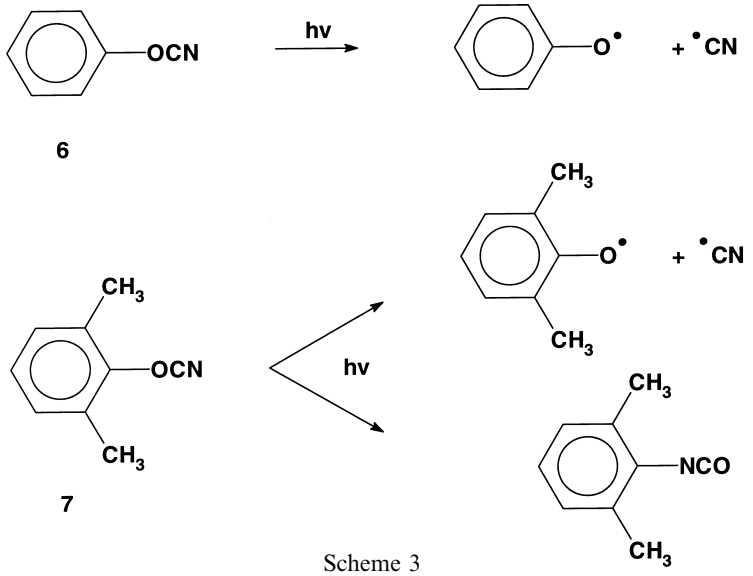
were phenol, phenoxycyclohexane and cyclohexyl cyanide. These products are explained by a radical scission of the OCN group in phenoxy and cyano radicals as has been reported by Hara *et al.* [11].

2,6-Dimethylphenyl cyanate (**7**) also showed this type of fragmentation as suggested by the formation of 2,6-dimethylphenol and cyclohexyl cyanide as photolysis products. 2,6-Dimethylphenyl isocyanate was produced in large amounts together with 1,3-dimethylbenzene. This finding would suggest a radical mechanism for the photoisomerization. However, 2,2′,6,6′-tetramethylbiphenyl, which would be expected as the recombination product of free 2,6-dimethylphenyl radicals, was not found at all. Further investigations are currently in progress to elucidate the mechanism of the isomerization reaction. The main photoreactions of the cyanates (**6**) and (**7**) are summarized in Scheme 3.

Photocrosslinking of the copolymers (**5a**) and (**5b**)

In our experiments, films with 0.5 and 1 μm thickness were irradiated with 254 nm UV light. The low absorbance of the copolymers (**5a**) and (**5b**) in the spectral region 230–300 nm ensured an almost uniform light intensity throughout the depth of the films.

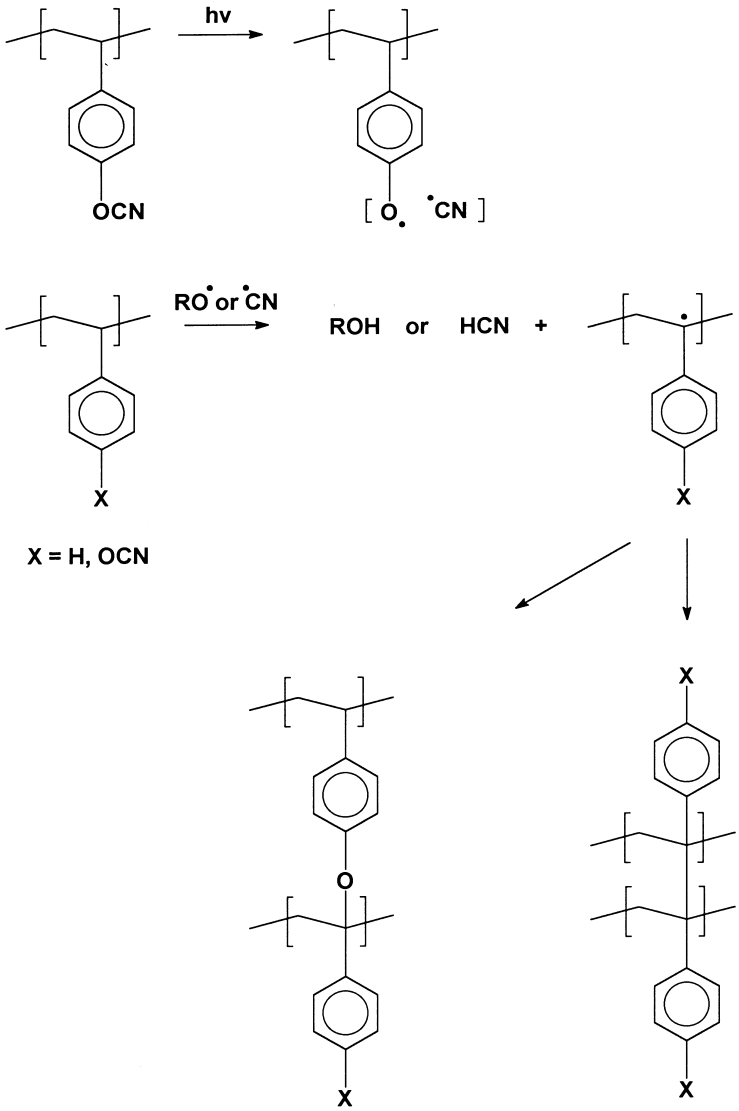
The copolymers (**5a**) and (**5b**) became crosslinked after UV irradiation. In Fig. 3 plots of the insoluble fraction W vs the irradiation dose E are shown. By extrapolation of the sensitivity curves to the onset of gelation, the gel doses E_g were obtained. In the case of copolymer (**5a**), a value of $E_g = 40$ mJ·cm^{-2} was found, whilst copolymer (**5b**) was considerably less photoreactive ($E_g = 220$ mJ·cm^{-2}). This was unexpected, because both copolymers (**5a**) and (**5b**) were comparable regarding their content of OCN substituents, average molecular weight $\bar{M}_W$ and UV



Scheme 3

absorbance at the irradiation wavelength 254 nm. To explain this situation it is necessary to consider the photoreactions occurring in the polymers under irradiation.

In the IR spectrum of copolymer (**5a**) the absorbance of the split OCN band at the center wavenumber 2252 cm^{-1} decreased after prolonged irradiation. From the experiments with phenyl cyanate (**6**) it can be concluded that the irradiation of copolymer (**5a**) yields polymer-bound phenoxy and free cyano radicals. Accordingly, the crosslinking of copolymer (**5a**) occurs via radical intermediates. Possible photocrosslinking reactions for copolymer (**5a**) are shown in Scheme 4.



Scheme 4

The situation is more complex for copolymer (**5b**), in which the OCN substituent is neighbored by methyl groups. The OCN band with a center wavenumber of 2258 cm^{-1} quantitatively disappears after irradiation and is replaced by an intensive band at 2276 cm^{-1} (see Fig. 4). This spectral change and the experiments with 2,6-dimethylphenyl cyanate (**7**) in solution prove the formation of isocyanate groups as the main photolysis product.

Polymer-bound phenoxy and free cyano radicals, which are also produced during UV irradiation, explain the crosslinking of copolymer (**5b**) (see Scheme 4). Our experiments with 2,6-dimethylphenyl cyanate (**7**) did not evidence that photoisomerization of the OCN groups proceeds via free phenyl and OCN radicals as intermediates. Accordingly, radicals of this type will play a minor role in the photocrosslinking process.

Two reasons may be responsible for the lower

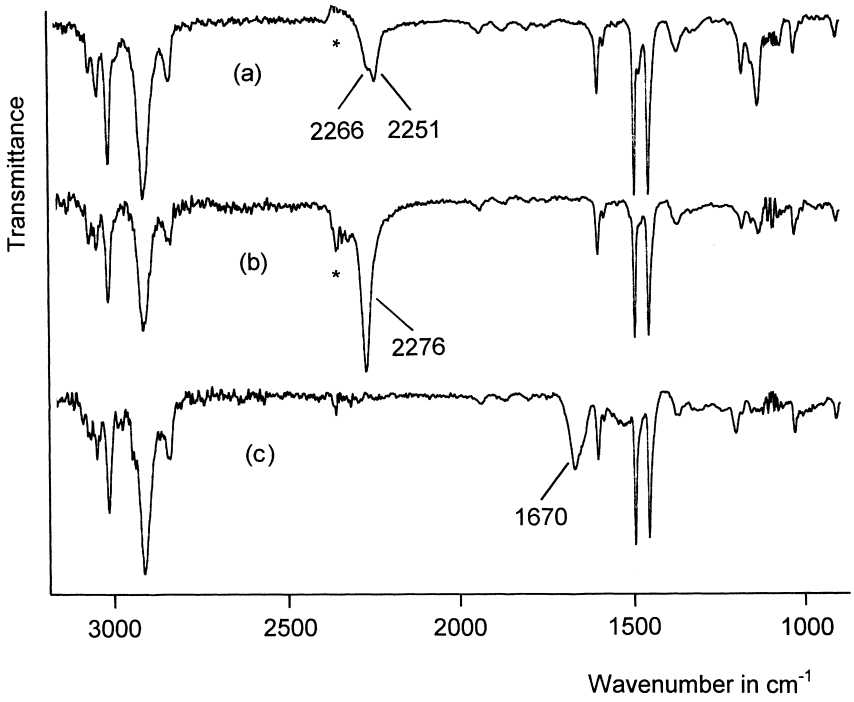


Fig. 4. IR spectra of copolymer (**5b**): (a) before irradiation; (b) after irradiation: (c) after irradiation and subsequent treatment with benzylamine. The IR band marked with * originates from CO_2.

photosensitivity of copolymer (**5b**) compared with copolymer (**5a**): on the one hand, a large fraction of the light energy absorbed in copolymer (**5b**) is consumed for the isomerization reaction which does not seem to yield free radicals. Consequently, the yield of crosslinking is lowered. On the other hand, steric hindrance makes the phenoxy radicals produced in copolymer (**5b**) less effective as to hydrogen abstraction which also decreases the yield of crosslinks.

Reaction of irradiated films of copolymer (**5b**) with amines

Isocyanates undergo addition reactions with alcohols and amines to form urethanes and ureas, respectively. The formation of isocyanate groups in irradiated films of copolymer (**5b**) provides an opportunity for selective functionalization of the irradiated zones.

We irradiated a 1.0 μm thick film of copolymer (**5b**) cast onto a CaF_2 plate until transformation of the OCN into NCO groups was almost complete. Subsequently, the plate was immersed in a mixture of benzyl amine, chloroform and *n*-hexane (3:3:10 by volume) for 20 min. After this treatment severe changes in the IR spectrum were observed (see Fig. 4). The NCO band at 2276 cm^{-1} had disappeared quantitatively, and instead a new band located at 1670 (C═O) cm^{-1} was observed. The spectroscopic changes prove the formation of benzyl urea groups in the irradiated film.

CONCLUSIONS

From our results the following conclusions are drawn. The new monomers 4-vinylphenyl cyanate (**4a**) and 2,6-dimethyl-4-vinylphenyl cyanate (**4b**) are comparatively stable compounds which can be employed in free radical polymerizations.

The styrene copolymers (**5a**) and (**5b**) of the monomers (**4a**) and (**4b**) are photosensitive and become crosslinked under 254 nm UV irradiation. With gel doses E_g of 40 $mJ \cdot cm^{-2}$ (copolymer **5a**) and 220 $mJ \cdot cm^{-2}$ (copolymer **5b**), they are negative resists of moderate sensitivity.

The cyanate ester (OCN) groups in copolymer (**5b**) isomerize to isocyanate (NCO) groups during UV irradiation. The irradiated films of copolymer (**5b**) readily undergo addition reactions with amines. This can be applied for surface modification procedures (e.g. silylation or coloring).

The thermal curing of the copolymers (**5a**) and (**5b**) with 4-nonylphenol as catalyst yields highly crosslinked networks. However, comparatively long curing times must be applied in order to achieve conversion of the cyanate ester groups into cyanurates.

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