Preparation of Photoresist Polymer by a Photoreactive Monomer Containing N,N-Diethyldithiocarbamate Group

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Synopsis

A novel photosensitive monomer with a pendant photoreactive diethyldithiocarbamoyl group, VBDC, was synthesized and copolymerized with some vinyl monomers by AIBN. The copolymers obtained have efficient photocrosslinking abilities, and are thermally stable. Therefore, there was no loss of dithiocarbamoyl group during radical polymerization, and the polymerization proceeded through vinyl group. The degree of photocrosslinking was proportional to the concentration of the photosensitive group, but photosensitivity of the polymer was not. Water-soluble photoreactive copolymers, VBDC with AAm or MA, were also prepared. AAm copolymer has a good photosensitivity by only 3 mol % VBDC incorporation. Photocrosslinking yields of these polymers depend on the viscosity of original polymers except in the case of low concentration of VBDC. The relation between copolymer composition and glass transition temperature was also investigated. From the investigation of T_g, it was concluded that the copolymer structure largely affected on ΔT_g. The mechanism of photocrosslinking was studied by photodecomposition of benzyl N, N-diethyldithiocarbamate, and the result that the decreases of sulfur content clearly related to photocrosslinking points was also obtained.

INTRODUCTION

Recently, much attention has been paid to photofunctional polymers, because they are widely used as photoresists, printing plates, and so on.

Polymers with pendant cinnamate ester have been used as photosensitive polymers for their excellent thermal stability and photoreactivity.[1] However, the results of polymerization of vinyl cinnamate indicated that the radical polymerization of vinyl cinnamate proceeds not only through normal vinyl polymerization mechanism but also through cyclopolymerization mechanism or crosslinking reactions, the latter occupying a major portion.

Other kinds of photoreactive polymers are polymers which have photodissociable or photoinitiating group in side chain. Typical examples of this kind are benzoin ethers,[2,3] substituted acetophenones,[4] and arylketones.[5,6]

In a continuation of our interest in photochemical reactions of polymer systems, we set up to use an initiator which has relatively good thermal stability but which is labile when irradiated with UV or visible light. In this meaning, dialkyldithiocarbamates are one of the most interesting compounds and are currently used as photoinitiators for the iniferter system in radical polymerization.[7] It has been known that dithiocarbamate derivatives, when exposed to UV light, produce polymerization-initiating radicals through the C—S bond cleavage and that polymers containing the dithiocarbamoyl moiety

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(—SCSNR$_2$) are effective as photosensitive resins, which were usually pre-
pared by polymer reactions.[8] Last year, we reported the synthesis and
polymerization of 4-vinylbenzyl N, N-diethyldithiocarbamate (VBDC).[9] The
photochemical reactivity and the initiator of graft polymerization were also
investigated. In the present work, we report the preparation of VBDC
copolymers and its photochemical behavior as a new photosensitive polymer
containing photodissociable diethyldithiocarbamoyl moieties.

If only the vinyl group in the monomers can be subjected to polymerization,
linear and highly photosensitive polymers which preserve the photoreactive
structure should be produced quantitatively, and this requirement is satisfied
in the case of VBDC. In addition, properties of photocrosslinkable polymers
obtained by polymer-modifying reactions are always dominated by that of
original polymer; this restriction, however, can be solved by using monomers
which have photoreactive group in side chain, since the character of copoly-
mers are controlled by copolymerization reactivity. The polymers of VBDC
thus produced generally showed very excellent properties as photocrosslink-
able polymers.

Moreover, a water-soluble photoresist polymer is desirable, because organic
solvents are expensive and sometimes toxic, and easier treatment is preferred.
Therefore, we prepared water-soluble photoreactive copolymers with acryla-
mide (AAm) or methacrylic acid (MA).

VBDC polymers thus obtained were investigated as to such properties as
photosensitivity, degree of photocrosslinking, and physical behavior.

EXPERIMENTAL

Materials

Solvents were purified by distillation just before use. 2, 2'-Azobisisobu-
tyronitrile (AIBN) was recrystallized twice from methanol. The monomers
obtained commercially were purified by recrystallization or distillation
according to ordinary method. 4-Vinylbenzyl N, N-diethyldithiocarbamate
(VBDC) was prepared by the reaction of 4-chloromethylstyrene with sodium
N, N-diethyldithiocarbamate.[9]

Polymerization and Copolymerization of VBDC

Radical polymerization and copolymerization of VBDC were carried out in
benzene, dimethylsulfoxide (DMSO), or ethanol (EtOH) in the presence of
AIBN. The required amount of VBDC, AIBN, and solvent·were charged into
Pyrex ampules, which were then degassed by conventional freezing and
thawing techniques, and sealed off under vacuum. Polymerizations were
carried out in a thermostatted bath for a given time. After the polymerization,
in the case of VBDC homopolymer and copolymers with styrene (St), methyl
methacrylate (MMA), acrylonitrile (AN), or vinyl acetate (VAc), the contents
of the ampules were poured into a large amount of hot methanol (MeOH).
The precipitated polymers were purified by a reprecipitation method from a
chloroform–hot MeOH system. Copolymers with MA were purified by precipi-
tation from DMSO into H$_2$O, and in the case of AAm copolymers, purification
was carried out from an H$_2$O–EtOH system. Copolymer compositions were

determined by elemental analyses of sulfur. The intrinsic viscosities of polymers were obtained at 30°C using an Ubbelohde viscometer in a suitable solvent for each polymer.

Photocrosslinking of Polymers

In order to examine the ability of photocrosslinking, thin films of VBDC homopolymer or copolymers were prepared as follows: A benzene solution of the homopolymer or copolymers was cast on glass slide, and then these films were dried standing overnight at room temperature. The thin films obtained (thickness ca. 10–20 μm) were irradiated by a 100 W high pressure mercury lamp (Toshiba SHL-100UV-2) from a distance of 10 cm at room temperature. After the irradiation, the glass slides were placed in benzene for 5 h to develop the crosslinked films. The yields of photocrosslinking were estimated by the weight of the films which remained on glass slide after development.[10]

Characterization of the Polymers

IR spectra were measured on a Nihon Bunko IRA-2, and ^{1}H-NMR spectra were obtained on a Hitachi R600 spectrometer. DSC analyses were carried out with a Rigaku PTC-10A at a heating rate of 10°C/min under air.

RESULTS A͡N͡D DISCUSSIONS

Preparations of Photosensitive Polymers

As reported in the previous paper, VBDC is easily synthesized by the reaction of p-chloromethylstyrene and sodium diethyldithiocarbamate.[9] The radical copolymerizations of VBDC with several vinyl comonomers were carried out in the presence of AIBN under the various conditions shown in Table I. As can be seen in this table, polymerization proceeded easily, and each copolymer was obtained with the expected composition. The copolymers with St, MMA, VAc, and AN were soluble in benzene, chloroform, DMSO, and DMF. In order to obtain water-soluble photoresist resins, copolymerization of VBDC with MA or AAm was performed. However, the copolymer with AAm dissolved only in water at little amount of VBDC composition, and in the case of MA copolymer, only NaOH aqueous solution (3 wt %) dissolved the copolymer.

In the case of VBDC homopolymer, the viscosity was low compared with that of MMA, St, or AN copolymer produced under the same conditions.

Figure 1 shows IR spectra of VBDC monomer and homopolymer. They agreed nicely except for the absorption at 1630 cm^{-1} caused by C=C stretching, and ^{1}H-NMR spectra of VBDC monomer and homopolymer agreed with each other except for the signals of CH$_2$=CH— protons of styrene. In addition to IR and NMR spectra, sulfur analyses of VBDC and homopolymer agreed well within experimental error. Moreover, the insoluble product was not generated in the radical polymerization.

From these results, the polymers consisted of ordinary chain structures by opening of the double bond of VBDC the same as styrene, and no reaction proceeded on the photosensitive side chain during the radical polymerization.

TABLE I
Copolymerization of VBDC with Vinyl Monomers[a]

Run	[VBDC] (mol/L)	[M$_2$] (mol/L)	Solvent	Time (h)	Yield (%)	VBDC in[b] copolymers (mol %)	[η][c] (dL/g)
Homo	0.91	—	Benzene	49.6	73.0	100.0	0.13
St-70	1.01	St (0.43)	DMSO	38.0	67.5	70.5	0.31
St-50	0.91	St (0.91)	Benzene	49.6	71.0	50.3	0.19
MMA-70	1.09	MMA (0.47)	DMSO	15.0	43.0	74.0	0.48
MMA-10	0.52	MMA (4.68)	DMSO	9.0	63.1	14.1	1.96
AN-50	0.53	AN (0.53)	DMSO	7.5	42.6	49.6	0.34
VAc-90	0.54	VAc (4.88)	Benzene	30.5	10.1	88.2	0.11
AAm-2	0.04	AAm (1.96)	EtOH	3.0	77.1	2.6	0.19[d]
MA-40	0.50	MA (1.50)	EtOH	18.0	89.8	39.6	0.36[e]

[a] Polymerized with AIBN (0.01M) at 60°C.
[b] Determined by elemental analysis of sulfur.
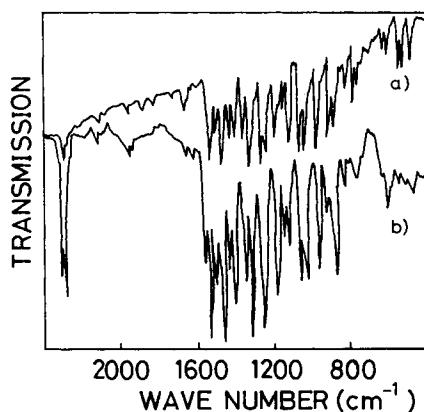[c] 30°C in benzene.
[d] 30°C in H$_2$O.
[e] 30°C in DMSO.

Fig. 1.   IR spectra of VBDC monomer and homopolymer.

TABLE II
Photocrosslinking of VBDC Polymer Films[a]

Run	Original films Wt (mg)	Thickness (μm)	[η] (dL/g)	Yield[b] (%)
Homo	3.9	4.0	0.13	53.8
St-70	4.0	10.0	0.31	88.9
MMA-10	4.3	25.6	1.96	100.0
AN-50	4.4	18.6	0.34	92.7
VAc-88	4.1	9.4	0.11	50.6
AAm-2	4.5	18.0	0.19	53.3
MA-40	4.5	15.0	0.36	81.1

[a]UV irradiated for 2.5 h from 10 cm distance.
[b]Benzene-insoluble films.

Then, we investigated the photochemical reactivity of the diethyldithiocarbamoyl group on polymers.

Photocrosslinking of VBDC Polymers

As in Table II, high photocrosslinking yields were obtained in every run, i.e., neither copolymer composition nor the kind of comonomer used had any effect. Though VBDC homopolymer has a high concentration of the photocrosslinkable diethyldithiocarbamoyl group, the yield of photocrosslinking is lower than that of copolymers. The low molecular weight of VBDC homopolymer ([η] = 0.13) may have caused the low photocrosslinking yield.

In the copolymerization of VBDC with VAc as shown in Table I, the copolymer obtained was VBDC-rich composition by the poor reactivity of VAc. Therefore, the yield of photocrosslinking is low as same as VBDC homopolymer.

In the case of copolymerization with AAm, the content of VBDC is restricted below 3 mol % to be dissolved in water. As a result, the photocrosslinking yield result is low. When we considered low VBDC content, being as little as 3%, photocrosslinking of this copolymer occurred effectively, and the
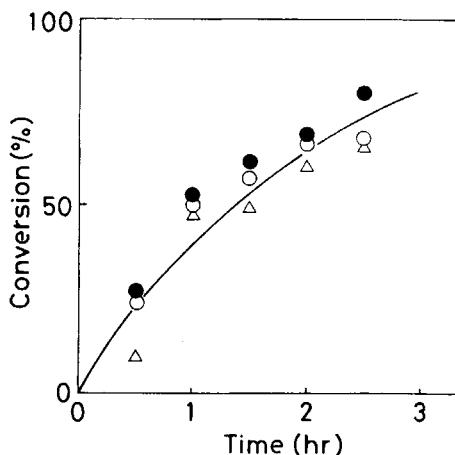
Fig. 2. Time–conversion curve of St–VBDC copolymer films change into crosslinked films by UV irradiation. [VBDC] (mol %), [η] (dL/g): (○) 94.0, 0.29; (●) 70.0, 0.31; (△) 31.0, 0.32.

yield of the crosslinked polymer is obtained as much as in the case of VAc-88 copolymer and homopolymer. On the other hand, MA copolymer dissolved in water even at VBDC composition as high as 40 mol %, because MA changed to sodium salt in the course of aftertreatment. The resulting MA copolymer showed a good photocrosslinking yield like the St–70 copolymer by 40 mol % VBDC content.

Relation between Polymer Composition and Photocrosslinking Yields

The photocrosslinking yields of VBDC–St copolymers whose molecular weights are nearly the same are not affected by the copolymer composition within the range as shown in Figure 2.

Figure 3 shows the relation between the photocrosslinked yield after 1 h irradiation and intrinsic viscosity of the copolymers. The reactivities of three
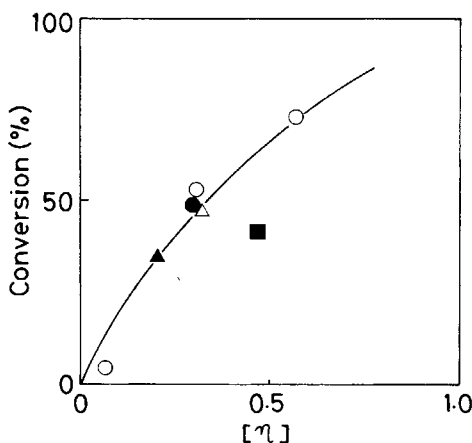

Fig. 3. Effect of [η] on the photocrosslinking of St–VBDC copolymer films. [VBDC] (mol %): (●) 94; (○) 70; (▲) 50; (△) 31; (■) 16.
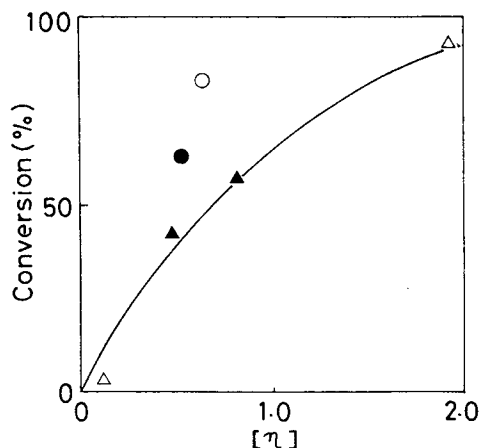
Fig. 4. Effect of $[\eta]$ on the photocrosslinking of MMA–VBDC copolymer films. [VBDC] (mol %): (●) 74; (○) 52; (▲) 18; (△) 14.

different viscosities of St-70 copolymers were plotted against intrinsic viscosity and a curve was obtained. Other kinds of VBDC copolymers whose VBDC contents were 94, 50, and 31 mol % nicely matched this reactivity–viscosity relation curve. Therefore, the photocrosslinking yield of VBDC–St copolymer depends on viscosity, i.e., molecular weight, of the original copolymer. However, in case the VBDC content in copolymer was 16 mol %, the reactivity decreased less than this relation. The results in the case of the VBDC–MMA copolymer indicated a similar tendency to VBDC–St copolymer, and Figure 4 shows this result. These results indicated that the yields of crosslinked polymer depend on the molecular weight of photoreactive polymers.

Mechanism of Photocrosslinking

The effect of concentration of the photoreactive group was estimated on the photocrosslinking reaction of the polymer films, since the sensitivity and resolving power depend largely on degree of photocrosslinking of polymer. Therefore, the evaluation of physical properties of the photosensitive polymer was performed as follows:

First, the glass transition temperature (T_g) was used as a measure of modification of physical properties of polymer. The T_g value suggests much valuable information on the polymer, since there are a lot of investigations that show that crosslinking reactions decrease free volume and raise the T_g of polymer. It is also known that the increment of T_g (ΔT_g) is estimated by the average molecular weight of segments between crosslinking points.[11] Thus, the measurements of the ΔT_g were carried out for the VBDC homopolymer and St copolymer. These results are shown in Table III. The more the mole fraction of VBDC increases, the more does the ΔT_g decrease against our expectation except for VBDC homopolymer. These results indicate that the numbers of photocrosslinking points are not there so much to increase ΔT_g. Consequently, it may be said that the ΔT_g is affected little by the number of crosslinking points, but is largely controlled by the copolymer structure. In other words, the ΔT_g of VBDC copolymer increases with the content of the styrene unit which has higher T_g than that of VBDC. However, in the case of VBDC

TABLE III
Photocrosslinking Reaction of VBDC Polymer Films[a]

Run	Original films				Crosslinked films[b]				
	[VBDC] (mol %)	S_0 (%)	T_{g0} (°C)	$[\eta]$ (dL/g)	Yield (%)	S (%)	T_g (°C)	ΔS^c (%)	ΔT_g^d (°C)
Homo	100	24.31	67.0	0.13	53.8	20.30	79.0	4.00	12.0
St-94	94	23.85	70.6	0.29	77.0	21.75	77.5	2.75	6.9
St-70	70	20.94	77.5	0.31	88.9	18.14	85.0	2.80	7.5
St-50	50	17.40	75.0	0.20	59.3	16.92	90.5	0.48	15.5
St-31	31	13.00	70.8	0.33	75.0	11.72	92.5	1.28	21.7
St-17	17	8.12	74.0	0.47	69.5	7.20	102.0	0.92	28.0

[a] UV irradiated for 2.5 h from 10 cm distance.
[b] Benzene-insoluble films.
[c] $\Delta S = S_0 - S$.
[d] $\Delta T_g = T_{g0} - T_g$.

homopolymer, every structural unit has a photoreactive dithiocarbamoyl group and many crosslinking reactions would occur as the result. Therefore, the number of crosslinking points may affect ΔT_g.

Consequently, in order to discuss the mechanism of photoreaction of diethyldithiocarbamoyl group in VBDC, it is important to evaluate the amount of photocrosslinking. For this purpose, the elemental analyses of sulfur of polymer films before irradiation and after development supply convenient and useful information. The results are shown in Table III.

First of all, a model reaction was carried out by using monomeric analog. Benzyl N, N-diethyldithiocarbamate was irradiated in chloroform for 12 h. After the reaction, the reaction mixture was analyzed by thin layer chromatography,[12] and benzylchloride and N, N, N', N'-tetraethylthiuramdisulfide (TD) were confirmed as the main products:

$$PhCH_2SC(S)NEt_2 \xrightarrow[\text{in CHCl}_3]{h\nu} PhCH_2Cl + \tfrac{1}{2}Et_2NC(S)SSC(S)NEt_2$$
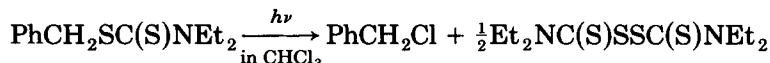
From this photodecomposition reaction, it is clearly seen that the bond cleavage reaction occurred at the C—S bond at the benzyl position. Therefore, the same cleavage reaction as model reaction was supposed to proceed in the photocrosslinking, and the TD generated was removed in the development process. As the results, the sulfur content of the polymer film decreased after the development.

From these facts, it may be said that the decrease of S% in polymer film means the generation of crosslinking points. As clearly seen from Table III, the amounts of decreased sulfur contents after the irradiation ($S_0 - S$), that is, generations of crosslinking points, are proportional to VBDC content in copolymer structure.

From these results, the degree of crosslinking increased with the increasing of the photoreactive group in the polymer film. However, the amount of insoluble product in polymer film which was produced by photocrosslinking did not relate to the composition of VBDC copolymer, because the insolubility was generated by little crosslinking. On the other hand, a too low concentration of the photosensitive group induces the yield to decrease.

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