Synthesis of Poly(vinyl ether) Optical Plastics by Cationic Copolymerization of Tricyclodecane Vinyl Ether with Functionalized Vinyl Ethers

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ABSTRACT: Cationic copolymerizations of tricyclodecane vinyl ether (8-vinyloxytricyclo[5.2.1.0^{2,6}]decane, TCDVE, with vinyl ethers containing a functional group such as urethane linkage, acrylate group, and methacrylate group, as a comonomer were carried out to obtain poly(vinyl ether) plastics for optical use. With the hydrogen chloride/zinc chloride initiating system, the homopolymerization rates of these monomers were markedly different from each other, but the reaction rates of each monomer in the copolymerizations were almost identical. All the obtained copolymers displayed unimodal and narrow molecular weights distributions (MWDs). These facts show that the copolymers are most likely to have randomness with respect to monomer sequences. The copolymers obtained with BF$_3$OEt$_2$ as an initiator, in contrast, had relatively high molecular weights ($M_n = 21,900 - 37,200$) and broad MWDs ($M_w/M_n = 4.10 - 6.31$), which are rather suitable for molding of plastic materials. For the copolymer with the pendant urethane linkages, the existence of hydrogen bonding via urethane linkages among the polymer chains was detected. For the copolymers with the pendant acrylate or methacrylate group, exothermic peaks due to cross-linking reaction were observed at around 150°C on the heating scan during the DSC measurement and therefore, they formed cross-linked polymers during the molding process above this temperature. Both the hydrogen bonds and the cross-linkages provide the copolymers with good processability and hardness. The optical properties of these copolymers were excellent and similar to those of poly(TCDVE). The transparency (86–91%) and refractive index (1.53–1.54) of these molded samples were similar to those of conventional optical plastics such as poly(methyl methacrylate) (PMMA) and polycarbonate (PC), whereas their specific gravity (1.08–1.12) and water absorption (0.08–0.16%) were significantly lower than those of PMMA and PC. The thermal decomposition temperatures of all the copolymers were 298–369°C, indicating their good thermal stability. © 2012 Wiley Periodicals, Inc. J Appl Polym Sci 000: 000–000, 2012

**Key words:** cationic polymerization; vinyl ether; copolymers; tricyclodecane; optical plastics

INTRODUCTION

Vinyl ethers are important cationically polymerizable vinyl monomers[1–3] and manufactured in industry mainly by the addition of alcohols to acetylene developed by Reppe.[4] Among the vinyl ethers with a variety of substituents,[5–8] a recent new series covers vinyl ethers with an aliphatic polycyclic substituent.[9–12] Poly(vinyl ether)s with linear alkyl side chains are usually sticky liquids or gum at room temperature because of their low glass transition temperatures (T_g) [examples of T_g of poly(alkyl vinyl ether)s; alkyl: methyl, -34°C; ethyl, -42°C; *n*-butyl, -55°C; *n*-octyl; -80°C],[13] and hence are difficult to use as commodity plastics. In contrast, the polymer of vinyl ether with a tricyclodecane unit (8-vinyloxytricyclo[5.2.1.0^{2,6}]decane), TCDVE, exhibited high T_g (e.g., ~ 100°C) and high thermal stability (e.g., thermal decomposition temperatures (T_d) = ~ 350°C).[9] Poly(TCDVE) was found to form transparent plastic resins with relatively high refractive index and high hydrophobicity.[10] One drawback of poly(TCDVE) plastics is, however, that they are rather brittle for use in optical plastics. This was overcome to some extent by introduction of flexible chains into the polymer side chains by copolymerization of TCDVE with a vinyl ether with a linear alkyl group (e.g., *n*-butyl vinyl ether; NBVE).[10] The poly(TCDVE-*stat*-NBVE) was indeed less brittle than the homopolymer of TCDVE and still had similar optical properties to those of the homopolymer of TCDVE.[10]

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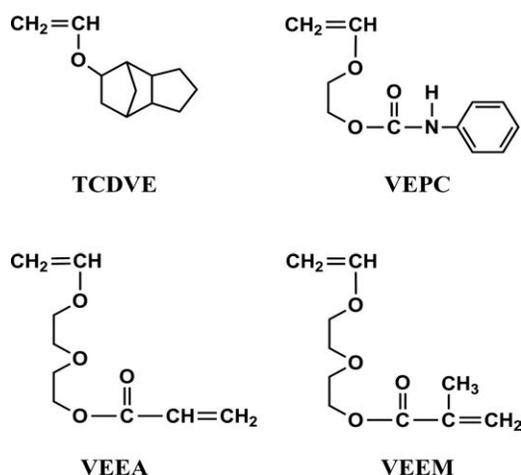
Scheme 1 Structures of vinyl ethers used in this study.

In the present study, the authors aimed to develop new TCDVE-based poly(vinyl ether) optical plastics by copolymerizations of TCDVE with vinyl ethers containing a functional group—a urethane (2-vinyloxyethyl phenylcarbamate), VEPC, acrylate [2-(2-vinyloxyethoxy)ethyl acrylate], VEEA, or methacrylate group [2-(2-vinyloxyethoxy)ethyl methacrylate], VEEM—as comonomers (Scheme 1). The urethane linkages in the VEPC-containing copolymer may increase intermolecular polymer–polymer interaction via hydrogen bonding. The unsaturated groups in the VEEA- and VEEM-containing copolymers can undergo thermal polymerization to form cross-linked polymers. Both the roles of these functional side chains would increase the strength and hardness of the molded-polymer samples. The authors, in this study, report the cationic copolymerizations of TCDVE with vinyl ethers containing a urethane group or a (meth)acrylate group and the properties of the obtained copolymers for potential use in optical applications.

EXPERIMENTAL

Synthesis of 2-vinyloxyethyl phenylcarbamate

This monomer was synthesized by reacting phenyl isocyanate with 2-hydroxyethyl vinyl ether (HEVE) in a similar way to that described in a previous report.[14] The product monomer was purified by recrystallization from toluene. Isolated yield: about 36%. ^{1}H-NMR (DMSO-d_6, ppm): 9.77 (s, 1H, —NH—Ar), 7.45–6.98 (m, 5H, —NH—Ar), 6.54 (q, 1H, CH$_2$=CH—O—), 4.29 (t, 2H, —CH_2—O—CO—), 4.02, 4.24 (dd, CH_2=CH—O—), 3.91 (t, =CH—O—CH_2—CH_2—O—), ^{13}C-NMR (DMSO-d_6, ppm): 153.4, 151.5, 139.0, 128.7, 122.4, 118.3, 87.3, 66.1, 62.7. Anal. calcd for $C_{11}H_{13}NO_3$: C 63.76, H 6.32, N 6.76; found: C 63.84, H 6.30, N 6.76.

Other materials

TCDVE (mixtures of the isomers)[9] and HEVE[15] were supplied by Maruzen Petrochemical (Tokyo, Japan) and purified as described in the previous reports.[9,15] VEEA and VEEM were supplied by Nippon Shokubai (Osaka, Japan), dried over sodium sulfate, and distilled over tert-butylcatechol under reduced pressure. Solvents (methylene chloride, toluene, and diethyl ether) and tetrahydronaphthalene (internal standards for gas chromatography) were purified as described in the previous report.[14] HCl (4.0 M solution in dioxane), BF$_3$OEt$_2$ (distilled) and ZnCl$_2$ (1.0 M solution in diethyl ether) were all supplied by Aldrich and used as received.

Procedures

Polymerizations were performed under a dry nitrogen atmosphere in a glass-tube equipped with a three-way stopcock as already reported.[9,14] Copolymers were prepared by polymerizing of TCDVE and a comonomer (VEPC, VEEA, or VEEM) simultaneously. Monomer conversions of TCDVE and the other vinyl ethers were determined from their residual concentrations measured by gas chromatography with tetrahydronaphthalene as an internal standard. The polymerizations were terminated by the addition of an excess amount of ammoniacal methanol. To work up the product polymers, the reaction mixtures were diluted with CH$_2$Cl$_2$, washed with 10 wt % aqueous sodium chloride to remove initiator residues, evaporated to dryness under reduced pressure, and vacuum-dried to give product polymers. For the measurements of optical and physical properties, the polymers were further purified by reprecipitation in methanol from tetrahydrofuran.

Measurements

The molecular weight distributions (MWDs) of the polymers were measured by gel permeation chromatography (GPC) in chloroform (at a 1.0 mL/min flow rate) at 40°C on a Shimadzu LC-10AD chromatograph equipped with four polystyrene gel columns (Shodex K-805 x 1 and K-804 x 3) and a Shimadzu RID-6A refractive index detector. The number-average molecular weight (M_n) and polydispersity ratio [weight-average molecular weight/number-average molecular weight (M_w/M_n)] were calculated from chromatograms on the basis of polystyrene calibration. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectra were recorded on a JEOL LA-500 instrument at room temperature with tetramethylsilane as an internal standard. IR spectra were recorded on a Nicolet MAGNA IR-560 spectrometer. Differential scanning calorimetry (DSC) was performed with a Rigaku
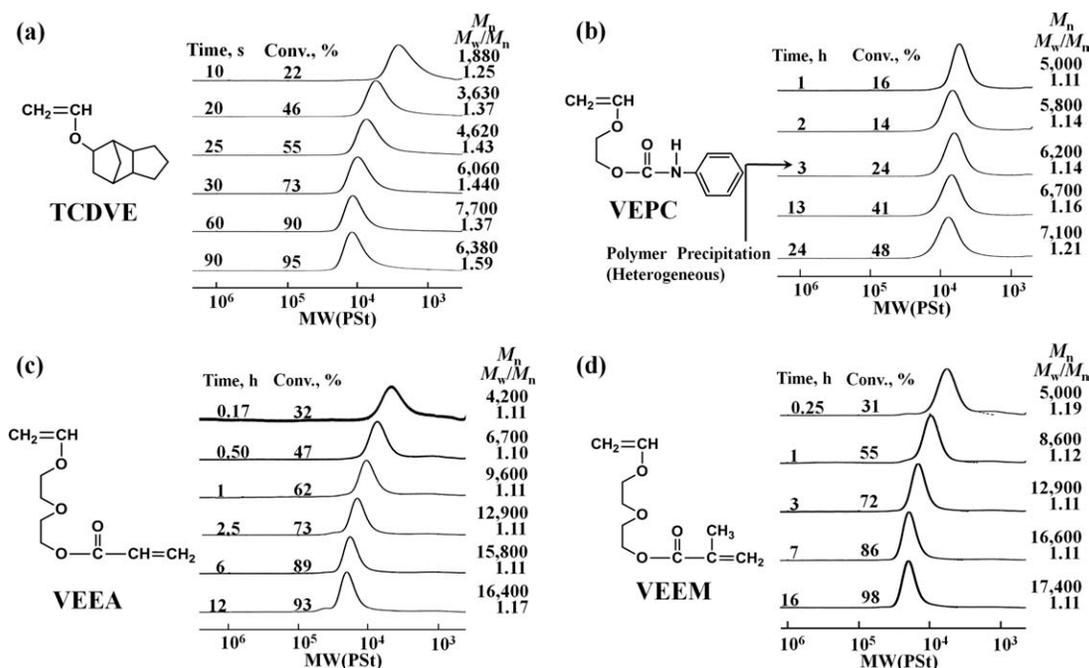
Figure 1 MWD curves of poly(vinyl ether)s obtained by the polymerizations of (a) TCDVE, (b) VEPC, (c) VEEA, and (d) VEEM with the HCl/ZnCl$_2$ system in toluene at $-30°C$: [monomer]$_0$ = 0.60 M; [HCl]$_0$ = 5.0 mM; [ZnCl$_2$]$_0$ = 5.0 mM.

Thermo Plus DSC 8230L. The temperature ranges were -20 to $+120°C$ for poly(TCDVE-*stat*-VEPC) and -20 to $+100°C$ for poly(TCDVE-*stat*-VEEA) and poly(TCDVE-*stat*-VEEM), and the heating and cooling rates were $5°C$/min. During the measurement, the sample was purged by nitrogen gas. The glass transition temperature (T_g) was defined as the temperature of the midpoint of change in heat capacity on the second heating scan. Thermogravimetric and differential thermal analysis (TG-DTA) was conducted with a Rigaku TG-DTA 8110 at a heating rate of $10°C$/min. The thermal decomposition temperature was defined as the temperature at which the sample lost 5% of its original weight. For measurements of the optical and physical properties of the polymers, the samples were molded by placing them in an As One AH-2003 hot press. The molding operation for poly(TCDVE-*stat*-VEPC) was conducted by heating at $125°C$ for 15 min at atmospheric pressure followed by heating at $115°C$ for 10 min at 20 MPa. The molding operation for poly(TCDVE-*stat*-VEEA) and poly(TCDVE-*stat*-VEEM) was conducted by heating at $70°C$ for 10 min at atmospheric pressure followed by heating at $70°C$ for 10 min at 20 MPa and the subsequent treatment at $160°C$ for 10 min at the same pressure. Specific gravity was measured by a Mirage SD-120L electronic densimeter. The light transmission factor (total transmittance) was measured by a Suga Test Instruments haze meter HGM-2K. Water absorption was calculated by comparing the weight of the rectangular samples (30 mm long, 30 mm wide, and 3 mm thick) in water at $23°C$ for

24 h (w) with the weight of the sample before the treatment (w_0) [water absorption = $(w - w_0)/w_0$]. The refractive index and Abbe number were measured by an Atago DR-M2 multi-wavelength Abbe refractometer using rectangular specimens (20 mm long, 8 mm wide, and 3 mm thick). The pencil hardness of these copolymers was determined on cast membranes according to JIS K5400.

RESULTS AND DISCUSSION

Copolymerization of TCDVE with functionalized vinyl ethers

The cationic homopolymerizability of all the vinyl ether monomers used in this study was first studied in toluene at $-30°C$ with the hydrogen chloride/zinc chloride (HCl/ZnCl$_2$) initiating systems, which are known to induce living cationic polymerization of TCDVE[9] as well as other vinyl ethers.[16,17] Because the polymerizations of vinyl ethers with functional substituents were often very slow (see below), relatively high ZnCl$_2$ initial concentration ([ZnCl$_2$]$_0$ = 5.0 mM) was used in this experiment. This concentration of ZnCl$_2$ is much higher than that suitable for living polymerization of TCDVE ([ZnCl$_2$]$_0$ = 0.5 mM).[9] Figure 1 shows the MWD curves of the obtained polymers as a function of time (or monomer conversion). For the polymerization of TCDVE [Fig. 1(a)], the reaction proceeded very fast with the conversion being 95% at 90 s and the polydispersity ratio (M_w/M_n) of the polymers was somewhat high
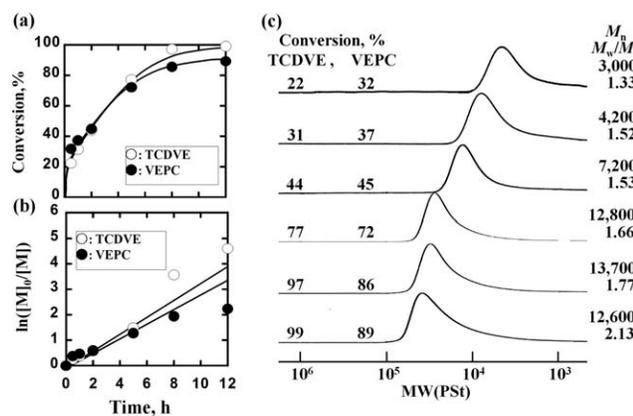
Figure 2 Copolymerization of TCDVE and VEPC with the HCl/ZnCl$_2$ system in toluene at $-30°$C: [TCDVE]$_0$ = [VEPC]$_0$ = 0.60 M; [HCl]$_0$ = 5.0 mM; [ZnCl$_2$]$_0$ = 5.0 mM; (a) time–conversion curve, (b) first-order plot, and (c) MWD curves of polymerization products.

Figure 3 Copolymerization of TCDVE and VEEA with the HCl/ZnCl$_2$ system in toluene at $-30°$C: [TCDVE]$_0$ = [VEEA]$_0$ = 0.60 M; [HCl]$_0$ = 5.0 mM; [ZnCl$_2$]$_0$ = 2.0 mM; (a) time–conversion curve, (b) first-order plot, and (c) MWD curves of polymerization products.

(1.25–1.59). In contrast, the polymerizations of the other three monomers proceeded at moderate rate. The acrylate or methacrylate-containing monomers, VEEA and VEEM, respectively, gave the polymers with narrow MWDs (1.1–1.2) almost quantitatively [Fig. 1(c) and (d)]. On the other hand, the polymerization of the urethane-containing monomer, VEPC, seemed to stop at around 50% conversion, probably because the reaction mixture turned heterogeneous by polymer precipitation after 24% conversion [Fig. 1(b)]. The narrow MWDs of the obtained poly(VEEA)s and poly(VEEM)s showed that only the vinyl ether group of the two vinyl functions in these monomers was selectively polymerized.

The polymerization rate of TCDVE was very high, reaching 100% conversion within a few minutes. In contrast, the other three monomers possessing polar functional groups required more than 10 h to attain nearly 100% conversion. In the case of copolymerization of these monomers, the large difference in monomer consumption rate could influence monomer sequences of the produced copolymers, with blocky sequences incorporated into the copolymer chains.

Therefore, the authors next investigated the consumption rate of each monomer during the copolymerizations of TCDVE with each of the three comonomers at the initial molar ratio of TCDVE : comonomer = 1 : 1. Figure 2(a) shows the time–conversion curves of the copolymerizations of TCDVE and VEPC (a vinyl ether with a urethane linkage), with the HCl/ZnCl$_2$ system in toluene at $-30°$C ([ZnCl$_2$]$_0$ = 5.0 mM). The reaction proceeded without an induction period and reached 100% monomer conversion without precipitation of the product polymers. Figure 2(b) depicts the first-order plots with respect to monomer. The reaction rates of both the monomers were almost identical from the early to middle stages of polymerization. The MWD curves of the product
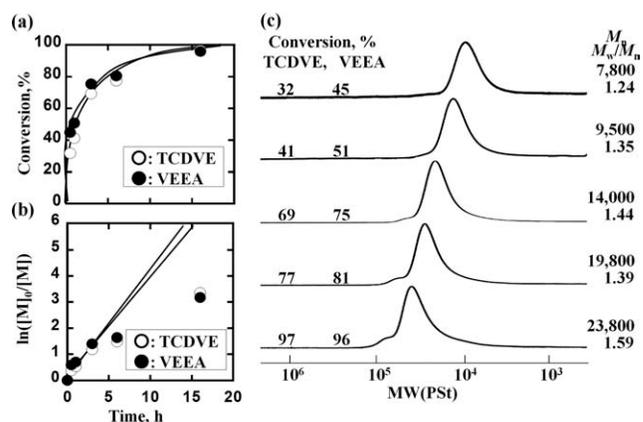
polymers are shown in Figure 2(c). The MWDs, although slightly broad, were unimodal throughout the copolymerization, which suggests that the formation of homopolymers is less likely. The combination of the similar consumption rate of the two monomers and the unimodal MWDs of the products, coupled with the fact that alternative copolymers very seldom produce in cationic vinyl polymerization,[18,19] shows the formation of the copolymers of TCDVE and VEPC with random monomer sequence.

Figures 3 and 4 show the results of copolymerization of TCDVE with VEEA (a vinyl ether with an acrylate group) or VEEM (a vinyl ether with a methacrylate group), respectively, under the same reaction conditions as those of the copolymerization with VEPC except for [ZnCl$_2$]$_0$ (2.0 mM). As in the case of the copolymerization with VEPC, these two copolymerizations proceeded to form quantitatively
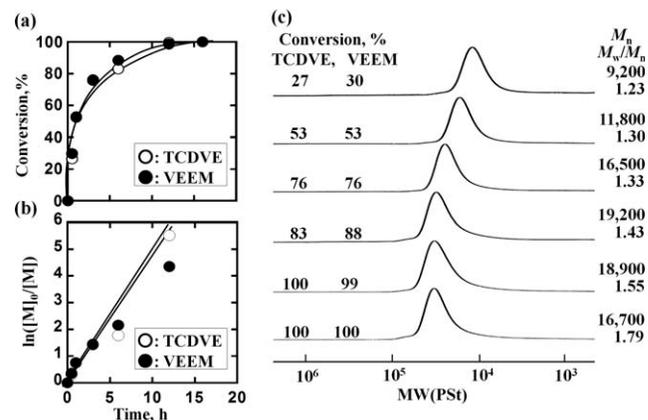

Figure 4 Copolymerization of TCDVE and VEEM with the HCl/ZnCl$_2$ system in toluene at $-30°$C: [TCDVE]$_0$ = [VEEM]$_0$ = 0.60 M; [HCl]$_0$ = 5.0 mM; [ZnCl$_2$]$_0$ = 2.0 mM; (a) time–conversion curve, (b) first-order plot, and (c) MWD curves of polymerization products.

TABLE I
Relative Polymerization Rate and ^{13}C NMR Chemical Shifts of Vinyl Ethers

	Relative rate[a]		^{13}C-NMR chemical shift,[b] δ (ppm)	
	Homopolymn[c]	Copolymn[d]	(CH₂=)	(=CH)
TCDVE	1.0	1.0	87.6	150.4
VEPC	0.00085	1.1[e]	87.5	151.7
VEEA	0.0095	1.1	86.9	151.8
VEEM	0.0074	1.0	86.8	151.9

[a] Polymerizations were carried out with HCl/ZnCl₂ in toluene at −30°C; relative polymerization rates were determined from the slope of the first-order plot with respect to each monomer.
[b] In CDCl₃ at room temperature.
[c] [Monomer]₀ = 0.60 M, [HCl]₀ = 5.0 mM, [ZnCl₂]₀ = 5.0 mM.
[d] [TCDVE]₀ = [comonomer]₀ = 0.60 M, [HCl]₀ = 5.0 mM, [ZnCl₂]₀ = 2.0 mM.
[e] [ZnCl₂]₀ = 5.0 mM.

the polymers with relatively narrow MWDs. The monomer consumption rates of TCDVE and the comonomer (VEEA or VEEM) were very similar to each other and the obtained polymers exhibited unimodal MWDs. These results suggest that both the copolymerizations produced the copolymers with rather random monomer sequences.

Close inspection of the MWD curves of poly (TCDVE-*stat*-VEEA)s shown in Figure 3(c), however, showed the existence of a small shoulder on the high molecular weight region of their MWD curves especially in the later stage of the copolymerization. This most likely comes from the reaction of the pendant unsaturated acrylate groups of the formed copolymers to give a very small amount of branched polymers. The minor extent of the similar reaction also may occur in homopolymerization of VEEA, as shown in Figure 1(c).

Table I compares the relative rates of each monomer as a function of the monomer substituent for homopolymerizations and copolymerizations. The relative rates were determined from the slope of linear first-order plots for monomer consumption in the early stage of the polymerizations [for examples, Figs. 2(b), 3(b), and 4(b) for the copolymerizations]. In the homopolymerizations, TCDVE exhibits the highest rate, 100–1000 times greater than those of the other three vinyl ethers containing functional groups. In contrast, the monomer consumption rate was almost the same during the copolymerizations. Table I also shows the ^{13}C NMR chemical shifts of the vinyl carbons (α and β) for the four monomers, which are considered to give a measure of their π-electron density. Both the α (CH=) and β (CH₂=) carbons show chemical shifts that are almost independent of the substituents. This implies that the electron densities on the vinyl double bonds of these monomers are similar to each other. The slow polymerization rate of the VEPC, VEEA, and VEEM in their homopolymerizations may be attributed to a decrease in concentration of free ZnCl₂ by possible complexation of the polar functional groups of the three monomers with the Lewis acid.[14]

Synthesis and molding of copolymers for optical plastics

After establishing the feasibility of cationic synthesis of the copolymers of TCDVE with functionalized vinyl ethers, VEPC, VEEA, and VEEM, the authors prepared these copolymers with high molecular weight and broad MWD, which are rather suitable for molding of plastic materials,[10] using BF₃OEt₂ as an initiator.

Thus, cationic copolymerizations of TCDVE with VEPC, VEEA, or VEEM were carried out with BF₃OEt₂ in toluene at −30°C for 1 h at a initial monomer feed ratio of TCDVE : comonomer = 8 : 2. Homopolymerization of TCDVE was also conducted to prepare a reference sample. Table II summarizes the results. All the reactions proceeded rapidly to give the polymer products quantitatively within 1 h. The number-average molecular weights of all the obtained copolymers were high and their MWDs

TABLE II
Thermal Properties of Poly(TCDVE)-based Copolymers and Poly(TCDVE)[a]

Polymer	Conversion (%)		M_n[b]	M_w/M_n[b]	T_g (°C)[c]	T_d (°C)[d]
	TCDVE	Comonomer				
Poly(TCDVE-*stat*-VEPC)	100	100	21,900	4.10	86	298
Poly(TCDVE-*stat*-VEEA)	100	100	37,200	6.31	45	351
Poly(TCDVE-*stat*-VEEM)	100	100	35,900	4.40	48	351
Poly(TCDVE)	100	0	83,000	2.64	107	369

[a] Polymerizations were carried out with BF₃OEt₂ in toluene at −30°C for 1 h: [TCDVE]₀ = 0.80 M; [comonomer]₀ = 0.20 M; [BF₃OEt₂]₀ = 2.0 mM.
[b] Measured by GPC with polystyrene calibration.
[c] Measured by DSC on second heating scan.
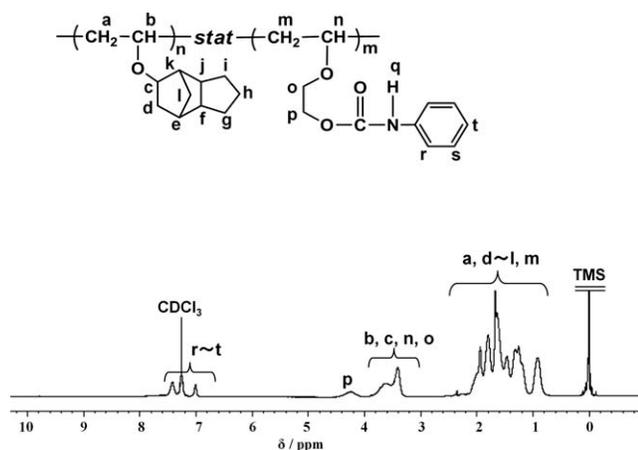[d] Measured by TG-DTA, 5% weight loss.

Figure 5 ^{1}H NMR spectrum (in CDCl$_3$) of poly(TCDVE-*stat*-VEPC) (M_n = 21,900; M_w/M_n = 4.10) obtained by the copolymerization of TCDVE and VEPC with BF$_3$OEt$_2$ in toluene at −30°C for 1 h ([TCDVE]$_0$ = 0.80 M; [VEPC]$_0$ = 0.20 M; [BF$_3$OEt$_2$]$_0$ = 2.0 mM).

were broad (M_n = 21,900–37,200, M_w/M_n = 4.10–6.31). Figures 5–7 illustrate ^{1}H NMR spectra of the obtained poly(TCDVE-*stat*-VEPC), poly(TCDVE-*stat*-VEEA), and poly(TCDVE-*stat*-VEEM), respectively, with peak assignments. All the spectra showed the key signals due to the functionalized pendants as well as the peaks of poly(TCDVE) main chain and side chains.[9] For example, the peak due to the urethane linkage (**p** in Fig. 5), the acrylate double bond (**s** and **t** in Fig. 6), and the methacrylate double bond (**t** in Fig. 7) are clearly observed. These facts show the incorporation of pendant urethane, acrylate, and methacrylate moieties into poly(TCDVE)-based polymers. The compositions of each monomer unit in the copolymers were determined with the peak intensity ratios of the methylene groups adjacent to the urethane or ester linkages [peak **p** in Fig. 5 for poly(-
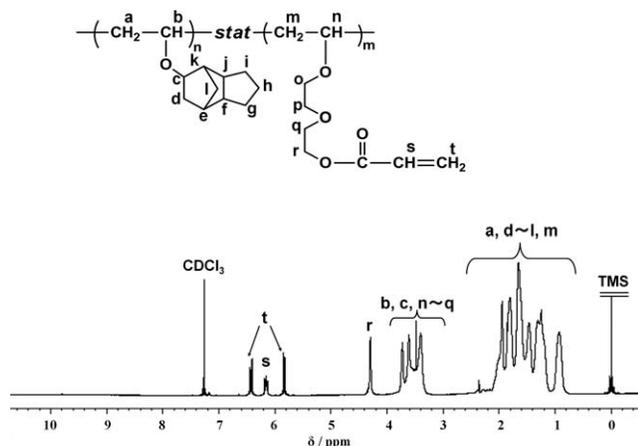

Figure 6 ^{1}H-NMR spectrum (in CDCl$_3$) of poly(TCDVE-*stat*-VEEA) (M_n = 37,200; M_w/M_n = 6.31) obtained by the copolymerization of TCDVE and VEEA with BF$_3$OEt$_2$ in toluene at −30°C for 1 h ([TCDVE]$_0$ = 0.80 M; [VEEA]$_0$ = 0.20 M; [BF$_3$OEt$_2$]$_0$ = 2.0 mM).
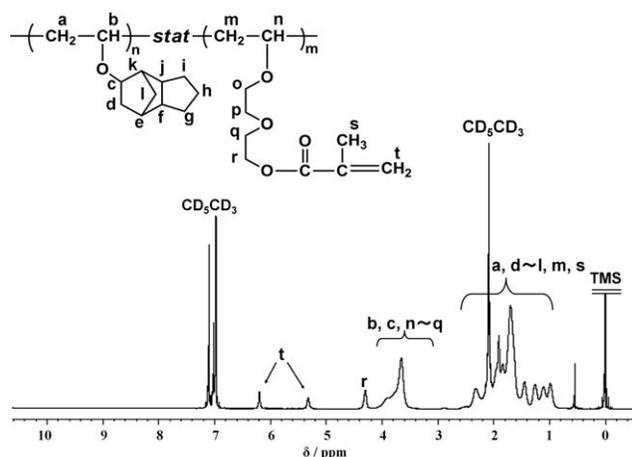
Figure 7 ^{1}H-NMR spectrum (in toluene-d_8) of poly(-TCDVE-*stat*-VEEM) (M_n = 35,900; M_w/M_n = 4.40) obtained by the copolymerization of TCDVE and VEEM with BF$_3$OEt$_2$ in toluene at −30°C for 1 h ([TCDVE]$_0$ = 0.80 M; [VEEM]$_0$ = 0.20 M; [BF$_3$OEt$_2$]$_0$ = 2.0 mM).

TCDVE-*stat*-VEPC); peak **r** in Fig. 6 for poly(-TCDVE-*stat*-VEEA); peak **r** in Fig. 7 for poly(TCDVE-*stat*-VEEM)] to the main and pendant groups adjacent to ether oxygen (a series of peaks at δ 3.2–4.0). The obtained composition ratios were [TCDVE] : [VEPC] = 0.817 : 0.183 for poly(TCDVE-*stat*-VEPC), [TCDVE] : [VEEA] = 0.824 : 0.176 for poly(TCDVE-*stat*-VEEA), and [TCDVE] : [VEEM] = 0.814 : 0.186 for poly(TCDVE-*stat*-VEEM). These composition ratios are in good agreement with the initial monomer feed ratios for each copolymerization: [TCDVE]$_0$: [comonomer]$_0$ = 0.80 : 0.20. This fact also confirmed random monomer sequences of the obtained copolymers.

Thermal properties of poly(TCDVE-*stat*-VEPC), poly(TCDVE-*stat*-VEEA), and poly(TCDVE-*stat*-VEEM) were measured by thermogravimetric and differential thermal analysis (TG-DTA) and differential scanning calorimetry (DSC). Figure 8 depicts the profile of TG-DTA of poly(TCDVE-*stat*-VEEM). The polymer displayed an exothermic peak at around
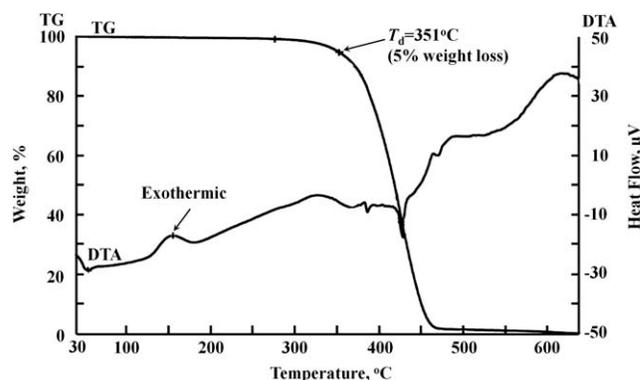

Figure 8 TG-DTA profile of poly(TCDVE-*stat*-VEEM) (M_n = 35,900; M_w/M_n = 4.40).
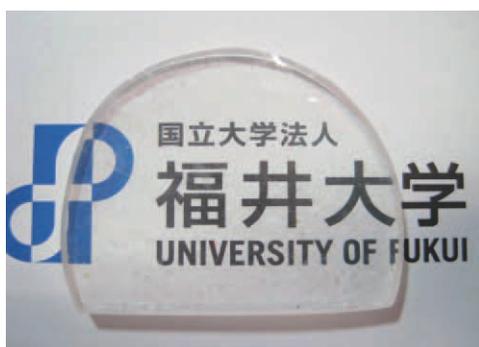
Figure 9 Photograph of the molded sample of poly(-TCDVE-*stat*-VEEA) ($M_n = 43,200$; $M_w/M_n = 4.00$).

150°C in DTA curve. This exothermic is most likely due to thermal cross-linking reactions of the methacrylate groups. Poly(TCDVE-*stat*-VEEA) also exhibited an exothermic peak at around 150°C in its DTA curve (thermogram is not shown). The glass transition temperature (T_g; measured by DSC) and thermal decomposition temperature (5% weight loss; T_d; measured by TG-DTA) of the three copolymers are shown in Table II, along with data for poly(TCDVE). The T_g's of the three copolymers are lower than that of poly(TCDVE) because of introduction of the flexible spacer chains between the functional pendant groups and the copolymer main chains [—CH$_2$CH$_2$— for poly(TCDVE-*stat*-VEPC); —CH$_2$CH$_2$OCH$_2$CH$_2$— for poly(TCDVE-*stat*-VEEA) and poly(TCDVE-*stat*-VEEM)], but still well above room temperature. The T_d's of the three copolymers are in the range of 300–350°C, indicating high thermal stability of these copolymers.

Figure 9 shows a picture of a typical molded sample of poly(TCDVE-*stat*-VEEA). The other copolymer samples also formed transparent molded plastics like the picture. Figure 10 illustrates IR spectra of poly(TCDVE-*stat*-VEPC) before and after the molding process. In both the spectra, the absorption due to the hydrogen-bonded urethane carbonyl groups (1710 cm^{-1})[20] coupled with the peak of the free car-
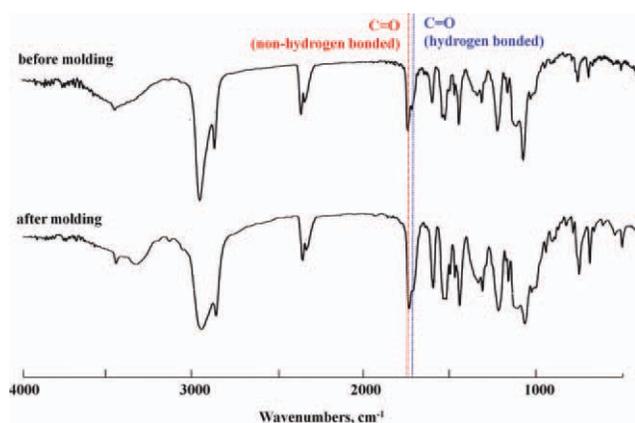

Figure 10 IR spectra of poly(TCDVE-*stat*-VEPC) ($M_n = 21,900$; $M_w/M_n = 4.10$) before and after molding process.
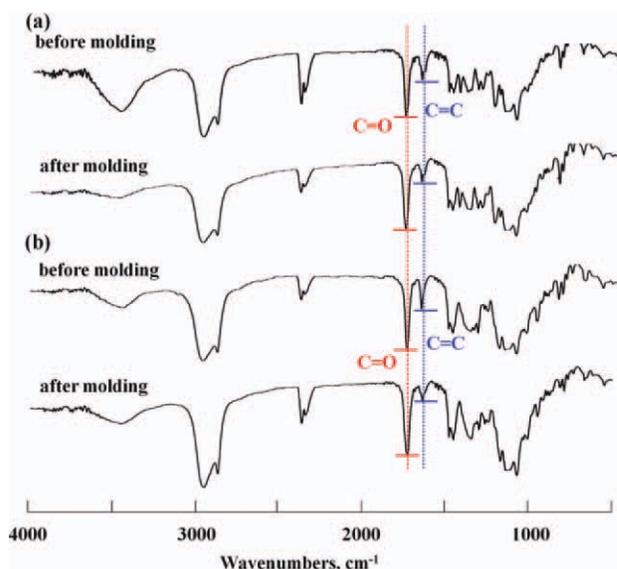

Figure 11 IR spectra of (a) poly(TCDVE-*stat*-VEEA) ($M_n = 37,200$; $M_w/M_n = 6.31$) and (b) poly(TCDVE-*stat*-VEEM) ($M_n = 35,900$; $M_w/M_n = 4.40$) before and after molding process.

bonyl groups (1730 cm^{-1}) was observed. Figure 11(a) and (b) depict of IR spectra of poly(TCDVE-*stat*-VEEA) and poly(TCDVE-*stat*-VEEM), respectively, before and after the molding process. For both the copolymers, the absorptions due to the C=C double bonds (1630 cm^{-1}) and the C=O carbonyl groups (1730 cm^{-1}) were observed. After the molding process at 160°C, the peak intensity of the double bonds was reduced when compared with the peak intensity of the carbonyl groups for both poly(TCDVE-*stat*-VEEA) [Fig. 11(a)] and poly(TCDVE-*stat*-VEEM) [Fig. 11(b)]. These results show the thermal polymerization of the pendant acrylates and methacrylates of the copolymers occurred during the molding process to give the cross-linked poly(TCDVE)-based polymers. The molded poly(TCDVE-*stat*-VEEA) and poly(TCDVE-*stat*-VEEM) were indeed insoluble in any organic solvents. The three copolymer plastics were apparently less brittle than the homopolymer of TCDVE, which is often damaged even by the molding process.[10] The strength of the poly(TCDVE-*stat*-VEPC) probably comes from intermolecular interactions via hydrogen bonds between the polymer chains, whereas that of poly(TCDVE-*stat*-VEEA) and poly(TCDVE-*stat*-VEEM) is due to cross-linking the polymer chains.

Physical properties of copolymers for optical use

Physical properties of poly(TCDVE-*stat*-VEPC), poly(TCDVE-*stat*-VEEA), and poly(TCDVE-*stat*-VEEM) for optical use were then measured. Table III shows a series of data of the physical and optical properties of the three molded copolymers along with those of poly(TCDVE) and conventional optical plastics—

TABLE III
Physical Properties of Poly(TCDVE)-based Copolymers[a] and Related Polymers

	Poly (TCDVE-*stat*-VEPC)	Poly (TCDVE-*stat*-VEEA)	Poly (TCDVE-*stat*-VEEM)	Poly (TCDVE)	PMMA[b]	PC[b]
Refractive Index	1.54	1.53	1.53	1.53	1.49	1.59
Abbe Number	52	50	51	62	58	31
Light transmission factor (%)	86	87	91	93	93	90
Specific gravity	1.12	1.11	1.08	1.08	1.19	1.19
Water absorption (%)	0.10	0.16	0.08	0.05	2.0	0.40
Pencil hardness	3H	3H	3H	2H	3H	B

[a] TCDVE : comonomer = 8 : 2 (molar ratio).
[b] Published report values.[21]

poly(methyl methacrylate) (PMMA) and polycarbonate (PC).[21] These copolymers exhibited good optical properties similar to those of poly(TCDVE). The refractive indices (1.53–1.54), Abbe number (50–52), and light transmission factors (86–91%) were similar to those of PMMA and PC. In contrast, the specific gravity (1.08–1.12) and water absorption (0.08–0.16%) of these copolymers were lower than those of PMMA and PC. The hardness of these copolymer samples was determined by pencil hardness test. The values for all the copolymers exhibited 3H point, even higher than that of poly(TCDVE) (2H point), and the same as that of PMMA, which is known to be a hard plastic. The high hardness of the three copolymers may be due to the existence of hydrogen bonds via urethane linkages [for poly (TCDVE-*stat*-VEPC)] or cross-linking points of acrylates and methacrylates [for poly(TCDVE-*stat*-VEEA) and poly(TCDVE-*stat*-VEEM)].

CONCLUSION

The present study demonstrates the synthesis of random copolymers by cationic copolymerization of TCDVE with vinyl ethers containing a urethane (VEPC), acrylate (VEEA), or methacrylate group (VEEM). Both the hydrogen bonds and the cross-linkages provide the copolymers with good processability and hardness for optical plastics. Their optical characteristics were similar to those of poly(TCDVE) and conventional optical plastics such as PMAA and PC, whereas their specific gravity and water absorption were significantly lower than those of PMMA and PC.

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