ELSEVIER

Polymer 43 (2002) 1189–1195

polymer

www.elsevier.com/locate/polymer

Radical copolymerization of 2-acetoxyacrylates with nitrile monomers and properties of the copolymers

H. Tanaka[a,*], T. Okazaki[a], Y. Tezuka[a], T. Hongo[a], Y. Takahashi[b]

[a]Department of Optical Science and Technology, Faculty of Engineering, Tokushima University, 2-1 Minamijosanjima, Tokushima 770-8506, Japan
[b]Department of Chemistry, Faculty of Science, Science University of Tokyo, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan

Received 11 July 2001; received in revised form 24 August 2001; accepted 16 October 2001

Abstract

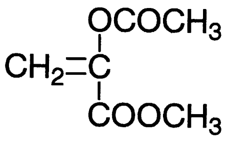
Radical copolymerization of captodatively (cd) substituted methyl and ethyl 2-acetoxyacrylates (MAA and EAA) with electron-withdrawing olefins including vinylidene cyanide and acrylonitrile is studied using azobisisobutylonitrile as a radical initiator at 60 °C, and the structure of copolymers is examined by ^{13}C NMR spectra. It is found that the copolymerization of MAA and EAA with vinylidene cyanide provides a 1:1 alternating copolymer with ε-tacticity of 0.540 and 0.517, respectively, but that with acrylonitrile gives a random copolymer containing a larger amount of acetoxyacrylate unit. Addition of zinc chloride to the copolymerization of MAA and acrylonitrile, however, leads to the increase of acrylonitrile unit contents in the copolymer. Dielectric constant, gas permeability, and deformation by elongation of the copolymer film of MAA and vinylidene cyanide are also examined.

Keywords: Radical polymerization; Captodative; Polymer sequence

1. Introduction

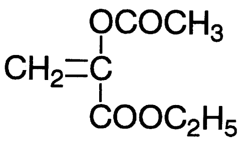
Polymers containing polar substituents including halogen and cyano groups are of interest in the development of advanced electrical and optical materials because of the large dipole moment expected from the polar substituents [1]. Nonlinear optical, piezoelectric, and pyroelectric properties have been observed in the polar polymers including fluorinated and cyanide polymers [2,3]. Vinylidene cyanide (VDCN) have often been employed in the preparation of high polar polymers as a useful starting monomer [4,5]. Homopolymer of VDCN, however, is unstable due to chain scission by atmospheric moisture even at ambient temperature and therefore rather impractical. Thus, the incorporation of VDCN unit into a polymer has been attempted by the copolymerization of VDCN with other various vinyl and diene monomers [6,7].

Captodatively (cd) substituted (geminal substitution of both electron-withdrawing and -donating groups on the same atom) olefins [8] are also polar monomers and expected to provide a high polar polymer through a radical polymerization in a mild condition. This paper deals with the copolymerization of cd olefins including methyl and ethyl 2-acetoxyacrylates (MAA and EAA) with nitrile monomers including VDCN and acrylonitrile (AN) in the presence and absence of Lewis acid including $ZnCl_2$. In addition, structures and properties of the copolymers are also studied.



$$CH_2{=}\overset{\displaystyle OCOCH_3}{\underset{\displaystyle COOCH_3}{C}}$$

MAA



$$CH_2{=}\overset{\displaystyle OCOCH_3}{\underset{\displaystyle COOC_2H_5}{C}}$$

EAA

2. Experimental

2.1. Materials

MAA was synthesized by the reaction of methyl pyruvate and acetic anhydride using *p*-toluenesufonic acid as a catalyst [9]. The resulting MAA was dried on CaH_2. In the preparation of EAA [10], methyl 2-trifluoroacetoxyacrylate (MTFAA) [11], and methyl 2-benzoyloxyacrylate (MBzA) [12], ethyl pyruvate, trifluoroacetic anhydride, and benzoic anhydride were used instead of methyl pyruvate or acetic anhydride used in the preparation of MAA. Methyl

---

* Corresponding author. Tel./fax: +81-88-656-9420.
E-mail address: tanaka@opt.tokushima-u.ac.jp (H. Tanaka).

0032-3861/02/$ - see front matter
PII: S0032-3861(01)00697-8

2-methoxyacrylate (MMOA) was prepared by the reaction of methyl 2,3-dibromopropionate and sodium methoxide according to the literature [13]. Purification of MMOA was carried out by fractional distillation of the eluent obtained through a pyrolysis of MMOA polymer at 270 °C which was independently synthesized by the radical polymerization of crude MMOA. VDCN was prepared by the pyrolysis of 1,1,3,3-tetracyano propane at 180 °C under reduced pressure and stored with P_2O_5 at −10 °C, in which the propane was provided by the condensation of malononitrile and formaline at 0 °C in ethanol in the presence of piperidine as a catalyst [14]. These olefins prepared were distilled just before use. Elemental analyses and ^{1}H NMR spectra of these monomers supported each structure. Commercially available (Wako Chemicals, Osaka, Japan) 2,2′-azobisisobutylonitrile (AIBN) and AN were used after recrystallization from ethanol and fractional distillation under reduced pressure, respectively. 2,2′-Azobis(2,4,4-trimethylpentane), $ZnCl_2$, and $SnCl_4$ were of a commercial grade and used without further purification.

2.2. Polymerization

Polymerizations were carried out in a sealed ampoule with shaking at given temperature. The ampoule, which contained the required amounts of reagents was degassed several times by a freeze–thaw method and then sealed under reduced pressure and placed in a constant temperature bath. The resulting polymer was isolated by pouring the contents of the ampoule into a large amount of methanol, other than the copolymerization of VDCN. A very small amount of hydrogen chloride was added into a methanol precipitant to remove the acid from the resulting polymer in the experiments with Lewis acid. In the copolymerization of VDCN, mixture of required amounts of cd olefins and AIBN was added into the VDCN contained in the ampoule which was cooled to −50 °C under nitrogen atmosphere. Then, the ampoule was quickly degassed several times by a freeze–thaw method and then sealed under reduced pressure and placed in a constant temperature bath. The resulting polymer was isolated by pouring the contents of the ampoule into a large amount of dry toluene. Copolymer composition was determined by elemental analysis for nitrogen.

2.3. Measurements

^{1}H and ^{13}C NMR spectra were measured in ca. 10 wt% deuterated-dimethylformamide (DMF-d_7) at 100 °C on a JEOL JNM-EX400 spectrometer at 400 and 100 MHz, respectively, using tetramethylsilane for ^{1}H NMR and DMF-d_7 (carbonyl carbon at 162.50 ppm) for ^{13}C NMR as an internal standard. Typical conditions in ^{13}C NMR spectrum measurements were as follows: sweep width = 20,000 Hz, data point = 32,000, pulse angle = 90°, pulse delay = 2.46 s, and accumulation = 20000 scans. FT-IR spectrum was recorded in film on JASCO FT/IR-8900 spectrometer. X-ray datum was obtained at ambient temperature on a Rigaku RAD-IIIA diffractometer with nickel-filtered CuK_α X-rays and a custom-built camera.

Number-average molecular weight (M_n) of a polymer was determined by SEC using a Tosoh HLC-8020 (columns: TSK gel-G7000HHR + G5000HHR + G3000HHR) in 0.1% DMF solution based on a standard polystyrene at 40 °C. Gas permeability was measured on JASCO Gasperm-100 at ambient temperature using 66 μm thickness membrane prepared by casting from CH_3NO_2. Cast membrane was immersed in methanol for about 48 h to eliminate residual CH_3NO_2 and then dried at 125 °C under vacuum for 24 h. Gas permeability coefficient (PC) was calculated by a steady-state gas permeation rate. The measurements were carried out under constant heating or cooling runs using a Toyo Seiki Seisakusho Rheolograph Solid controlled by a computer, in which Au electrodes were attached on both sides of P(MAA-*co*-VDCN) film which was prepared by casting from CH_3NO_2. Differential scanning calorimetry (DSC) was used to determine a glass transition temperature (T_g) with a heating rate of 10 °C/min on a Seiko DSC-22 thermal analyzer under a nitrogen stream.

3. Results and discussion

3.1. Copolymerization of cd olefins with VDCN

Copolymerization of cd olefins and VDCN was generally carried out with AIBN at 60 °C, and the result obtained using MAA as a cd olefin is listed in Table 1. On the basis of the result in Table 1, the copolymer composition curve of MAA (M_1) and VDCN (M_2) is depicted in Fig. 1. Monomer reactivity ratio (r) was calculated to be $r_1 = 0.20 \pm 0.03$, $r_2 = 0.13 \pm 0.02$, and $r_1 \times r_2 = 0.026$ according to the curve-fitting method and Kelen–Tudos plot based on the terminal model proposed by Mayo and Lewis, suggesting an alternating tendency in the copolymerization. These values are similar to those ($r_1 = 0.37$, $r_2 = 0.10$, and $r_1 \times r_2 = 0.04$) obtained by the copolymerization in similar conditions [15], although the propagation process in such copolymerization should be allowed to elucidate by other

Table 1
Copolymerization of MAA (M_1) and VDCN (M_2) in bulk with AIBN at 60 °C ([AIBN] = 5.0×10^{-3} mol l^{-1}, polymerization time: 1 h)

[M_1] in feed (mol%)	Yield (%)	*N*-content (%)	[M_1] in copolymer (mol%)
90	2.0	9.74	59.3
80	1.6	8.75	62.7
70	1.5	9.54	60.0
60	1.7	10.04	58.3
50	1.5	12.86	49.3
40	0.7	14.81	43.6
30	1.0	13.48	47.4
20	0.3	15.64	41.2

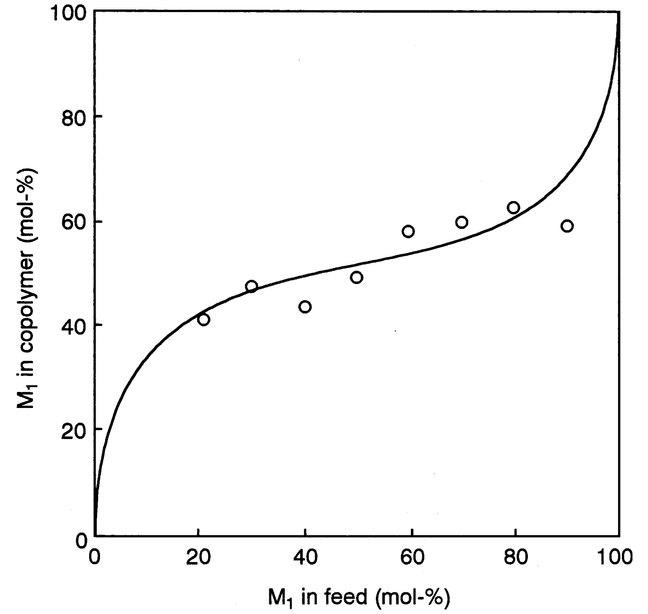


Fig. 1. Copolymer composition curve in the copolymerization of MAA (M_1) and VDCN (M_2) with AIBN in bulk at 60 °C. [AIBN] = 5.0×10^{-3} mol l^{-1}.

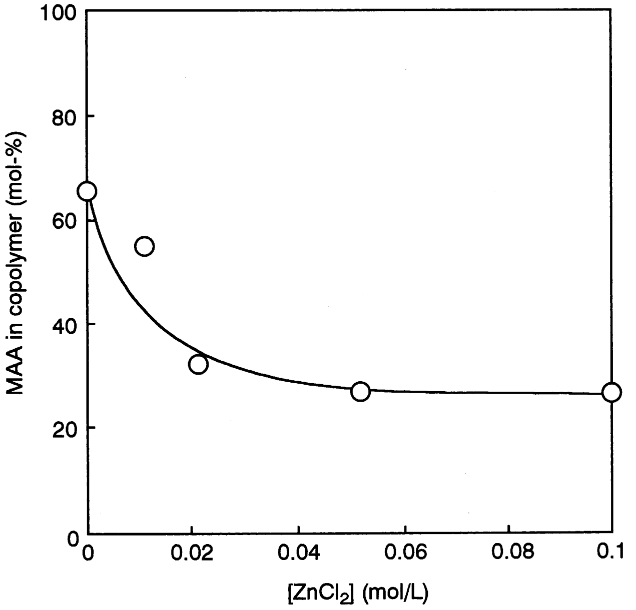


Fig. 2. Dependence of copolymer composition on the concentration of $ZnCl_2$ in the copolymerization of MAA and AN with AIBN in benzene at 60 °C. [MAA] = [AN] = 0.75 mol l^{-1}, [AIBN] = 5.0×10^{-3} mol l^{-1}.

propagation modes such as penultimate and penpenultimate models.

The copolymerization of MTFAA and VDCN (1:1 molar ratio) gave a polymer in 0.1 and 31.6% yields with AIBN (8.0×10^{-3} mol l^{-1}) at 70 °C and with 2,2′-azobis(2,4,4-trimethylpentane) (5.0×10^{-3} mol l^{-1}) at 110 °C, respectively. Both copolymers obtained contained nearly 90% VDCN unit in the structure. Such a high VDCN content in the copolymer is probably due to the Alfrey-Price *Q*-value of MTFAA ($Q = 0.65$) [11] smaller than that of MAA ($Q = 1.65$) [16]. Unfortunately, the solution turned instantly from colorless to brown just only by mixing VDCN with MMOA or MBzA, accompanying an exothermic reaction to fail in the copolymerization.

3.2. Copolymerization of MAA in the presence of Lewis acid

Lewis acids have been known to be a convenient and useful reagent to control a copolymer sequence in a radical copolymerization [17]. The mode of the radical copolymerizations of AN or methacrylonitrile and vinyl esters has been reported to be significantly varied with $ZnCl_2$ [18]. Fig. 2 shows the variation of the copolymer composition with the concentration of $ZnCl_2$ in the copolymerization of MAA and AN ([MAA] = [AN] = 0.75 mol l^{-1}) in the presence of $ZnCl_2$ at 60 °C. It is obvious that AN content in the copolymer increases with $ZnCl_2$ concentration as often seen in the conventional radical copolymerizations with Lewis acids [19].

Fig. 3 shows the copolymer composition curves for the copolymerization of MAA and AN in benzene with AIBN (5.0×10^{-3} mol l^{-1}) at 60 °C in the presence and absence of $ZnCl_2$. Incorporation of MAA unit into the copolymer has been reported to be dominant in the copolymerization of MAA (M_1) and AN (M_2) in the absence of Lewis acid, i.e. $r_1 = 0.99$ and $r_2 = 0.11$ [20]. Addition of $ZnCl_2$ to the copolymerization, however, changed the monomer reactivity ratio to be $r_1 = 1.19 \pm 0.05$ and $r_2 = 0.78 \pm 0.03$ for

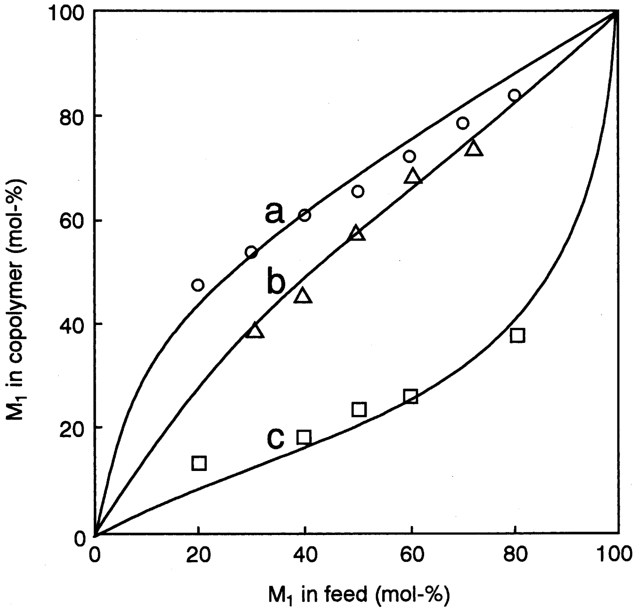


Fig. 3. Copolymer composition curves in the copolymerization of MAA (M_1) and AN (M_2) with AIBN in benzene at various concentration of $ZnCl_2$ at 60 °C. (a) [$ZnCl_2$] = 0, (b) [$ZnCl_2$] = 1.0×10^{-2} mol l^{-1}, and (c) [$ZnCl_2$] = saturated solution. [MAA] + [AN] = 1.5 mol l^{-1}, [AIBN] = 5.0×10^{-3} mol l^{-1}.

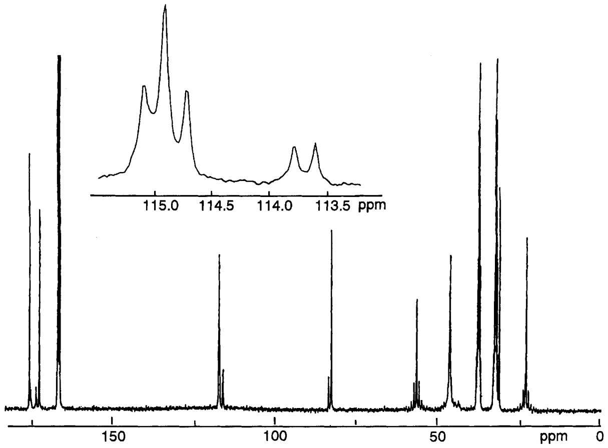


Fig. 4. ^{13}C NMR spectrum of P(MAA-*co*-VDCN) in DMF-d_7 and the expanded spectrum in the cyanide carbon region.

$[\mathrm{ZnCl_2}] = 1.0 \times 10^{-2}\ \mathrm{mol\,l^{-1}}$, and $r_1 = 0.02 \pm 0.01$ and $r_2 = 0.74 \pm 0.05$ for $[\mathrm{ZnCl_2}] =$ saturated solution (<[AN]). Generally, the more stable the radical, which was formed by the attack of a propagating radical to a monomer, the higher the reactivity of the monomer. Therefore, preferential stabilization of AN radical by complexation with $\mathrm{ZnCl_2}$ may bring about the enhancement of the reactivity of AN for the attack of a polymer radical, which results in an increase of AN contents in the copolymer. Addition of Lewis acid with higher acidity including $\mathrm{SnCl_4}$ into the mixed benzene solution of MAA and AN or MAA and VDCN accompanied an exothermic reaction and a color change from colorless to dark brown, resulting in no polymerization.

3.3. Structure of copolymers

^{1}H NMR spectrum of P(MAA-*co*-VDCN) (49.2% MAA content in the copolymer, $M_n = 2.1 \times 10^5$) represented the peaks at 2.23, 3.48, and 3.79 ppm due to the protons of methoxy, methylene, and acetyl groups, respectively. In order to discuss more quantitatively the sequence distribution, the tacticity was examined by ^{13}C NMR spectrum. Fig. 4 shows the spectrum of P(MAA-*co*-VDCN) in DMF-d_7 at 100 °C, in which the resonance lines around 21.10, 27.96, 43.52, 53.49, 79.84, 114.42, 168.16, and 170.81 ppm can be assigned to acetoxy methyl, VDCN unit quaternary, main chain methylene, methoxycarbonyl methyl, MAA unit quaternary, cyanide, methoxycarbonyl carbonyl, and acetoxy carbonyl carbons, respectively, and therefore all lines observed in Fig. 4 can be assigned to the carbon atoms in the copolymer and DMF-d_7 solvent. To confirm the sequence of the copolymer, resonances in the cyanide carbon region of P(MAA-*co*-VDCN) are expanded as shown in Fig. 4, in which three peaks at 114.75, 114.94, and 115.10 ppm and two peaks at 113.60 and 113.78 ppm can be assigned to MAA–VDCN–MAA and MAA–VDCN–VDCN sequences, respectively. VDCN–VDCN–VDCN sequence may be around 113.7 ppm according to the assignment for the copolymer of vinyl acetate (VAc) and VDCN [21]. Such peak, however, cannot be observed clearly in Fig. 4 probably because of the chemical shift of 113.7 ppm close to 113.60 and 113.78 ppm and negligible contribution of VDCN–VDCN–VDCN sequence. On the basis of the VDCN-centered triads, copolymerization parameters are calculated as listed in Table 2, in which the conditional probability P_{21} represents the addition of the propagating radical ending VDCN (M_2) toward MAA (M_1) monomer, N_2 represents the number-average sequence length of M_2, and σ_ε which is given by the ratio of peak intensity (I) in Fig. 4, $(I_{114.75} + I_{115.10})/(I_{114.75} + I_{114.94} + I_{115.10})$, corresponds to the ε-isotacticity.

Similarly, P_{12} and N_1 values for M_1 unit can be calculated from the MAA-centered triads which are determined from the acetyl methyl carbon of P(MAA-*co*-VDCN) in Fig. 5, in which the peak at 21.15 ppm is assigned to VDCN–MAA–VDCN triad and the peaks at 20.42 and 21.90 ppm may be assigned to VDCN–MAA–MAA triads including racemic and meso MAA–MAA forms, respectively, according to P(VAc-*co*-VDCN) [21]although detailed analysis is necessary for VDCN–MAA–MAA triads.

r_1 and r_2 in Table 2, determined from the peak intensities show an agreement with the experimental values, suggesting a reasonableness of the present NMR study. The value of $r_1 \times r_2$ obtained from the NMR analyses is close to zero, i.e. 0.02, indicating a preferential cross propagation in the copolymerization as demonstrated experimentally.

The σ_ε value of 0.540 obtained involves the atactic

Table 2
Copolymerization parameters for the copolymers of acrylates or vinyl acetate (M_1) and VDCN (M_2)

Parameters	P(MAA-VDCN)	P(EAA-VDCN)	P(VAc-VDCN)[a]	P(MMA-VDCN)[b]
P_{12}	0.873	0.852	0.895	0.966
P_{21}	0.917	0.947	0.940	0.932
r_1	0.184	0.157	0.116	0.036
r_2	0.095	0.062	0.064	0.073
N_1	1.195	1.174	1.116	1.036
N_2	1.091	1.056	1.064	1.073
σ_ε	0.540	0.517	0.506	0.495

[a] Data from Ref. [21].

[b] Data from Ref. [22].

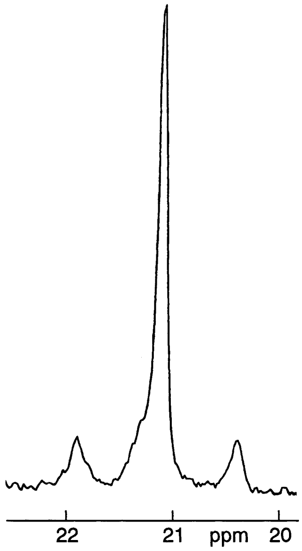


Fig. 5. Expanded spectrum in the acetoxy methyl carbon region of ^{13}C NMR spectrum of P(MAA-*co*-VDCN) in DMF-d_7.

structure of P(MAA-*co*-VDCN), and such a tacticity may result in the amorphous structure of the copolymer as already known in P(VAc-*co*-VDCN) [3]. X-ray diffraction of P(MAA-*co*-VDCN) demonstrates actually an amorphous structure, i.e. a broad diffraction at $2\theta = 11°$ with a half width of $2\theta = 30°$ at half height.

Fig. 6 represents the spectrum of P(EAA-*co*-VDCN) (52.5% EAA content in the copolymer, $M_n = 2.4 \times 10^5$) in DMF-d_7 at 100 °C, in which P(EAA-*co*-VDCN) was prepared by the copolymerization of equimolar amounts of EAA and VDCN with AIBN at 60 °C, in which the resonance lines around 13.44, 21.06, 29.05, 43.45, 63.18, 79.47, 115.06, 162.50, 170.84 ppm can be assigned to ethoxycarbonyl methyl, ethoxycarbonyl methylene, VDCN unit quaternary, main chain methylene, acetoxy methyl, EAA unit quaternary, cyanide, ethoxycarbonyl carbonyl, and acetoxy carbonyl carbons, respectively. In the expanded spectrum in the cyanide carbon region in Fig. 6, three peaks at 114.82, 115.06, and 115.24 ppm and two peaks at 113.70 and 113.91 ppm can be assigned to EAA–VDCN–EAA and EAA–VDCN–VDCN sequences, respectively, according to the assignment for P(VAc-*co*-VDCN) [21]. VDCN–VDCN–VDCN triad may appear around 113.8 ppm, but it can not be clearly detected. Fig. 7 shows the expanded spectrum in the ethoxy methyl carbon region of P(EAA-*co*-VDCN). Likewise with P(MAA-*co*-VDCN), three peaks at 13.27, 13.44, and 13.60 ppm, the peaks around 12.64 and 12.80 ppm, and the peaks around 14.10 ppm can be assigned to VDCN–EAA–VDCN and VDCN–EAA–EAA, and EAA–EAA–EAA sequences, respectively. Calculated P_{12}, P_{21}, r_1, r_2, N_1, N_2, and σ_ε values for P(EAA-*co*-VDCN) as well as those for P(VAc-*co*-VDCN) [21]and P(MMA-*co*-VDCN) [22] are also summarized in Table 2. Apparently, *P*, *r*, and *N* values calculated suggest an alternating tendency in their copolymerizations as also seen in Fig. 1. To provide more quantitative information on the compositional distribution, the theoretical compositions for all six triads were calculated using the monomer compositions and the conditional probabilities as shown in Table 3. As seen in Table 3, cd olefin or VDCN homotriad is almost negligible and the total sum

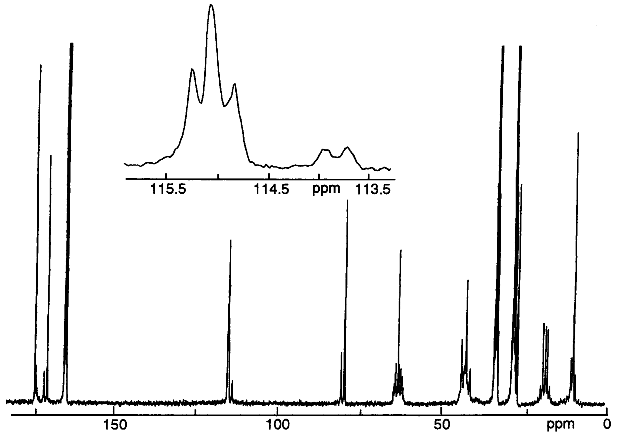


Fig. 6. ^{13}C NMR spectrum of P(EAA-*co*-VDCN) in DMF-d_7 and the expanded spectrum in the cyanide carbon region.

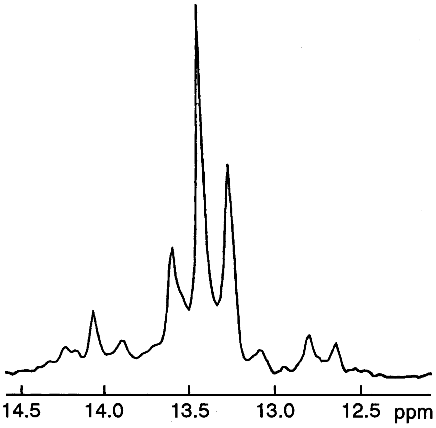


Fig. 7. Expanded spectrum in the ethoxycarbonyl methyl carbon region of ^{13}C NMR spectrum of P(EAA-*co*-VDCN) in DMF-d_7.

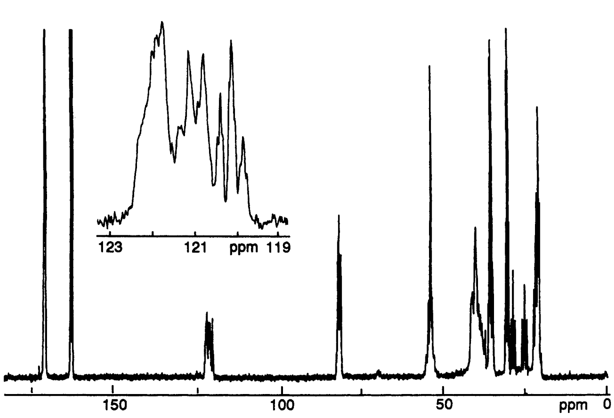


Fig. 8. ^{13}C NMR spectrum of P(MAA-*co*-AN) in DMF-d_7 and the expanded spectrum in the cyanide carbon region.

Table 3
Triad fractions calculated for the copolymers of acrylates or vinyl acetate (M_1) and VDCN (M_2)

Triads	Equation	Fraction			
		P(MAA-VDCN)	P(EAA-VDCN)	P(VAc-VDCN)[a]	P(MMA-VDCN)[b]
M_1–M_1–M_1	$(M_1)(1 - P_{12})^2$	0.004	0.002	0.006	0.001
M_1–M_1–M_2	$(M_1)(1 - P_{12})P_{12} + (M_2)P_{21}(1 - P_{12})$	0.142	0.133	0.096	0.033
M_1–M_2–M_1	$(M_1)P_{12}P_{21}$	0.415	0.442	0.442	0.435
M_2–M_2–M_2	$(M_2)(1 - P_{21})^2$	0.012	0.010	0.002	0.002
M_2–M_2–M_1	$(M_2)(1 - P_{21})P_{21} + (M_1)P_{12}(1 - P_{21})$	0.073	0.047	0.055	0.064
M_2–M_1–M_2	$(M_2)P_{21}P_{12}$	0.353	0.365	0.400	0.465

[a] Data from Ref. [21].
[b] Data from Ref. [22].

of the theoretical compositions for all the possible compositional triads is nearly equal to unity, i.e. 0.996 for P(MAA-*co*-VDCN) and 0.999 for P(EAA-*co*-VDCN).

^{13}C NMR spectrum of P(MAA-*co*-AN) (53.9% MAA content in the copolymer)[1] in DMF-d_7 at 100 °C shown in Fig. 8 represents peaks around 20.74, 21.69, 36.47–40.25, 53.39, 81.28, 120–123, 170.18 ppm which can be assigned to methyne, acetoxy methyl, main chain methylene, methoxycarbonyl methyl, MAA unit quaternary, cyanide, methoxycarbonyl carbonyl, and acetoxy carbonyl carbons, respectively. In the expanded spectrum in the cyanide carbon region in Fig. 8, three peaks around 120, 121, and 122 ppm can be assigned to AN–AN–AN, MAA–AN–AN, and MAA–AN–MAA sequences, respectively, according to P(ethyl methacrylate-*co*-AN) [23]. The absorptions around 120 ppm were further splitted into three peaks, i.e. 119.80, 120.16, and 120.38 ppm, which corresponded to *rr*, *mr*/*rm*, and *mm* sequences (*r*: *racemo* and *m*: *meso* forms), respectively, according to P(ethyl methacrylate-*co*-AN). The ratio of the peak intensities at 119.80, 120.16, and 120.38 ppm were nearly 1:2:1, suggesting an atactic structure of AN–AN–AN sequence in the copolymer.

3.4. Properties of copolymers

P(MAA) is insoluble in most of the organic solvents, but P(MAA-*co*-VDCN) is soluble in some organic solvents including acetone and can easily form a transparent film by casting from such solvents. It is possible to elongate P(MAA-*co*-VDCN) film as long as three times above glass transition temperature ($T_g = 150$ °C).[2] Fig. 9(a) and (b) show the non-polarized (a) and polarized (b) FT-IR spectra of P(MAA-*co*-VDCN) films not-elongated (a) and elongated (b). In the elongated polymer in Fig. 9(b), the absorption around 3000 cm^{-1} due to the main chain methylene is still remained in such difference spectrum between polarized spectra parallel and perpendicular to the deformation direction, suggesting the preferential orientation of the main chain to the elongation direction.

Fig. 10 shows the temperature dependence of the dielectric constant (ε) of P(MAA-*co*-VDCN) containing 49.2% MAA units. Apparently, ε increases gradually near 140–150 °C and goes up to 11.0 at 160 °C, i.e. glass transition temperature of the copolymer. It has been reported for P(VAc-*co*-VDCN) that the incorporation of flexible VAc unit in the ligid P(VDCN) backborn promotes the mobility of the polymer chain and allows to align the polar cyano groups so as to produce a large overall dipole moment, which results in the drastical increase of the ε value of

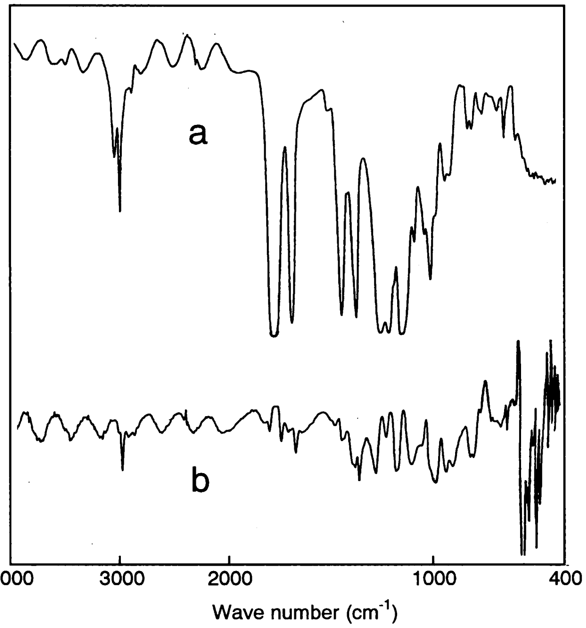


Fig. 9. FT-IR spectra of P(MAA-*co*-VDCN) film. (a) Non-polarized spectrum using not-elongated polymer film and (b) difference spectrum between polarized spectra parallel and perpendicular to the direction of the elongation, in which the film was elongated at 150 °C.

---

[1] P(MAA-AN) containing 53.9% MAA unit was prepared by the copolymerization of MAA and AN in benzene with AIBN (5.0×10^{-3} mol l^{-1}) at 60 °C in the presence of $ZnCl_2$ (1.0×10^{-2} mol l^{-1}).

[2] T_g of P(MAA-*co*-VDCN) was estimated to be 150 °C in film by DSC. For reference, T_g of P(MAA) film which was slowly casted from CH_2Cl_2 in the box filled with CH_2Cl_2 vapor over 2 days and finally dried in dry box for 2 h under vacuum at ambient temperature was estimated to be 162 °C by the measurement of the dynamic viscoelasticity although T_g seems to be dependent on the condition of sample preparation. In T_g measurement, an additional small peak appeared near ambient temperature probably due to a rotation of the side chain of the polymer.

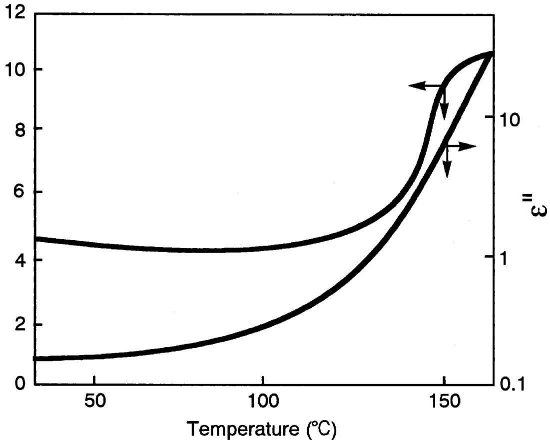


Fig. 10. Temperature dispersion of ε values of P(MAA-*co*-VDCN) at 10 Hz.

about 125 around its T_g [3]. The relatively small ε value of P(MAA-*co*-VDCN) above T_g may be contributed by the restriction of the side-chain orientation to one direction due to a steric hindrance of the bulky side-groups of P(MAA-*co*-VDCN) as known in P(MMA-*co*-VDCN) [3].

N_2 and O_2 gas permeability of P(VAc-*co*-VDCN) membrane has been reported to be influenced by the annealing time, i.e. density, of the polymer. P(MAA-*co*-VDCN) membrane has the density of $1.30\ \mathrm{g\ ml^{-1}}$ at 25 °C and higher than P(VAc-*co*-VDCN) membrane ($1.21\ \mathrm{g\ ml^{-1}}$ at 25 °C) [24]. Fig. 11 represents the plots of the amounts of the penetrant N_2 and O_2 gases for P(MAA-*co*-VDCN) membrane against time. From this Fig. 11, the amounts of penetrant at equilibrium and permeability coefficient (PC) for N_2 and O_2 gases are estimated to be 76.7 and $121.0\ \mathrm{ml(m^2\ 24\ h\ 76\ cmHg)^{-1}}$, and 7.7×10^{-13} and $1.22 \times 10^{-12}\ \mathrm{ml\ STP\ cm(cm^2\ s\ cmHg)^{-1}}$, respectively. The PC value of N_2 and O_2 gases for P(MAA-*co*-VDCN) membrane is much lower than that for P(VAc-*co*-VDCN) as well as other most of the polymers. The ratio of permeability coefficient $\mathrm{PC_{O_2}/PC_{N_2}}$ for P(MAA-*co*-VDCN) membrane is calculated to be 1.56, which is smaller than that for other conventional polymer membranes ($\mathrm{PC_{O_2}/PC_{N_2}} =$ ca. 3) and P(VAc-*co*-VDCN) membrane ($\mathrm{PC_{O_2}/PC_{N_2}} = 7.0$) [25]. These results obtained suggest that cd molecules provide a highly-stacked polar polymer which represents extremely low gas permeability and high T_g through a radical polymerization.

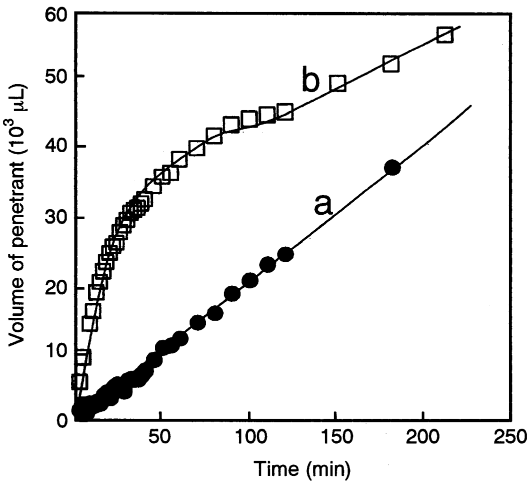


Fig. 11. Variation of volume of penetrant with time. (a) Oxygen and (b) nitrogen gases.

Acknowledgements

The authors are grateful to Dr N. Amaya of Nippon Oil and Fats Company Ltd. for the measurement of dynamic viscoelasticity and Mr H. Takechi of Tokushima Industrial Technical Center for the measurement of gas permeability.

References

[1] Gerhard-Multhaup R. Ferroelectrics 1987;75:385.
[2] Kawai H. Jpn J Appl Phys 1969;8:975.
[3] Miyata S, Yoshikawa M, Tasaka S, Ko K. Polym J 1980;12:857.
[4] Tasaka S, Inagaki N, Okutani T, Miyata S. Polymer 1989;30:1639.
[5] Greszta D, Mardare D, Matyjaszewski K. Macromolecules 1994;27:638.
[6] Montheard JP, Boinon B, Belfkira A, Carson EJ, Folt VL, Heller HJ, Stewart FD, Schmidt RF, Trumbll HL. J Am Chem Soc 1956;78:1670.
[7] Inoue Y, Kashiwazaki A, Maruyama Y, Jo YS, Chujo R, Seo I, Kishimoto M. Polymer 1989;30:698.
[8] Penelle J, Padias AB, Hall Jr. HK, Tanaka H. Adv Polym Sci 1992;102:73.
[9] Wolinky J, Nowak R, Vasileff R. J Org Chem 1964;29:3596.
[10] Thomas ML, Unruh CC. Ind Engng Chem 1958;50:1119.
[11] Tanaka H, Takeichi T, Hongo T. J Polym Sci, Part A, Polym Chem 1997;35:3537.
[12] Tanaka H, Yoshida S. Macromolecules 1995;28:8117.
[13] Ogata N, Nosakura S, Murahashi S. Bull Chem Soc Jpn 1970;43:2987.
[14] Ardis AE, Averill SJ, Gilbert H, Miller FF, Schmidt RF, Stewart FD, Trumbill HL. J Am Chem Soc 1950;72:1305.
[15] Montheard JP, Zerroukhi A, Ouillon I, Raihane M, Pham QT. J Macromol Sci, Pure Appl Chem 1997;A34:291.
[16] Tanaka H, Kikukawa Y, Kameshima T, Sato T, Ota T. Makromol Chem, Rapid Commun 1991;12:535.
[17] Bamford CH, Jenkins AD, Johnston R. Proc R Soc 1957;A241:364.
[18] Hall Jr. H, Padias AD, Chu G, Lee H-Y, Kalnin I, Sansone M, Breckenridge G. J Polym Sci, Part A, Polym Chem 1992;30:2341.
[19] Barton J, Borsig E, editors. Complexes in free radical polymerization. Amsterdam: Elsevier, 1988.
[20] Hongo T, Yoshida S, Yamada T, Tanaka H. Polym Int 1999;48:505.
[21] Jo YS, Inoue Y, Chujo R, Saito K, Miyata S. Macromolecules 1985;18:1850.
[22] Maruyama Y, Jo YS, Inoue Y, Chujo R, Tasaka S, Miyata S. Polymer 1987;28:1087.
[23] Kapor GS, Brag AS. J Polym Sci, Part A, Polym Chem 1991;29:479.
[24] Hachisuka H, Kito H, Tsujita Y, Takizawa A, Kinoshita T. J Appl Chem Sci 1988;35:1333.
[25] Pauly S. In: Brandrup J, Immergut EH, Grulke EA, editors. Polymer handbook, 4th ed. New York: Wiley, 1999. p. VI 435–49.