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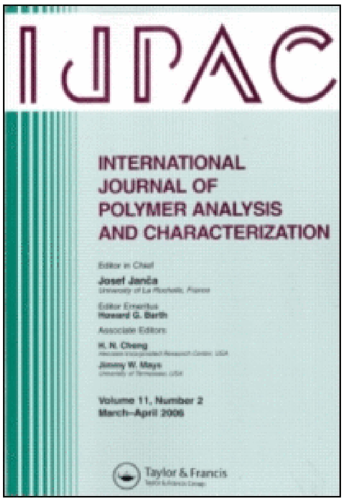

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Stabilization of Vinyl Chloride Monomer via Guest Adsorption Process in Cholic Acid Guest-Free Channel and Its Inclusion Polymerization

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Vinyl chloride monomer (VCM) was successfully introduced into cholic acid (CA) guest-free crystal by using the guest adsorption process at −15°C for three days, as clarified from thermal analysis, Fourier transform infrared spectroscopy (FT-IR), and X-ray diffraction (XRD) techniques. The VCM is stabilized in the CA channel as evidenced from the release temperature of VCM up to 40°C. Inclusion polymerization of CA-VCM host-guest adduct was achieved by γ-irradiation and postpolymerization. Under the conditions of dose rate 30 kGy and postpolymerization time for 40 days, the syndiotactic-rich PVC product

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with the molecular weight up to 4 × 10^5 daltons was obtained as confirmed by GPC, FT-IR, and ^{1}H-NMR.

Keywords: Vinyl chloride monomer, Cholic Acid, Guest adsorption, Inclusion polymerization, Polyvinyl chloride, Gamma-irradiation

INTRODUCTION

With rapid progress in polymer analysis and characterization, the properties of a polymer are known to be related to the structure at the molecular level. For the past few decades, the development of polymers has been challenged from the polymerization steps to achieve a well-defined structure by controlling the regularity, crystallinity, and morphology. Controlled structure polymers can be obtained, for example, by the use of a specific catalysis system and inclusion polymerization.

Inclusion polymerization is a space-dependent reaction that contributes to the synthesis of polymer with a controlled regularity. Up until now, a number of reports have been presented that utilize hosts such as urea, thiourea, cyclodextrin, and steroid compounds performing the inclusion polymerization of various vinyl monomers[1–9]. However, the inclusion polymerization of vinyl chloride monomer (VCM) is rarely reported since it has to deal with the low boiling point of VCM (−13°C), which limits the host-guest adduct stability.

Miyata et al. reported a series of cholic acid (CA) inclusion compound crystal structures and clarified the inclusion phenomena as a guest-responsive molecular assembly system[10]. The attraction of CA is that we can prepare a guest-free channel by excluding the guests from the CA host. By adsorption technique, another target guest can be inserted into the guest-free channel and the desired host-guest adduct can be achieved. As a result, CA is unique since it gives inclusion adducts either by direct recrystallization with guest or by guest adsorption into the guest-free CA host crystal.

The present work, thus, challenges the CA host channel for VCM guest. Up until now, there have been reports about the preparation of host and VCM adduct by soaking the host in liquefied VCM directly for perhydrotriphenylene (PHTP)[3], tris(*o*-phenylenedioxy) cyclotriphosphazene (TPP)[6], urea[7,8], and thiourea[9] hosts. Thus, the present work is aimed at preparing and clarifying the CA-VCM adduct through the process of a CA guest-free channel. The work also incorporates the inclusion polymerization of VCM in a CA channel in order to observe the polymer produced needs full stop.

EXPERIMENTAL

Materials

Cholic acid (AR grade) was purchased from TCI Co., Ltd. (Japan). Methyl methacrylate and solvents (AR grade) were purchased commercially and used without further purification. Vinyl chloride monomer (VCM) and commercial polyvinyl chloride (PVC) were supplied by Thai Plastics and Chemicals Public Company.

Preparation of CA Guest Free

Inclusion compound of CA with methyl methacrylate (MMA) was prepared by recrystallization to a CA-MMA adduct. Cholic acid guest-free crystal was obtained from evacuation of the CA-MMA adduct at 80°C for three hours.

Preparation of Cholic Acid–VCM (CA-VCM) Adduct

The obtained crystal was collected and kept in a tube. The liquefied VCM was gradually added into the tube, which was kept in liquid nitrogen. The tube was sealed in vacuo and left at −15°C for three days to allow the VCM to be adsorbed into the guest-free crystal CA before using.

Inclusion Polymerization of CA-VCM Adduct

The CA-VCM adduct was irradiated with γ-ray at 30 kGy under dry ice (−78°C) to initiate polymerization. The amount of γ-ray was varied from 10 to 40 kGy. The postpolymerization studies were carried out at −15°C for 2, 7, 14, and 40 days. After the postpolymerization, the CA-VCM adduct was taken out of the tube and washed using excess methanol 20 times to exclude polymer completely from the CA host. The product was dried under vacuum.

Characterization

The guest-releasing temperature of the CA-VCM adduct was observed by low temperature differential scanning calorimetry (DSC) using a Perkin Elmer Differential Scanning Calorimeter Pyris1 with a Perkin Elmer Liquid Nitrogen Cooling System CryoFill from −20°C to 120°C. A flow rate of 20 mL/min and a heating rate of 10°C/min were used. Infrared spectra of the CA-VCM adduct, CA-PVC adducts, PVC obtained, and the commercial PVC was obtained from a Bruker Equinox

55/S FT-IR spectrophotometer using the KBr pellet technique. The structures of the PVC obtained and commercial PVC were characterized by ^{1}H-NMR (nuclear magnetic resonance) at 270 MHz using a JEOL JNM-GSX 270 spectrometer FT-NMR. Powder X-ray diffraction (XRD) patterns were recorded over a 2θ of 5°–50° by a Rigaku RINT 2000 using CU Kα as an X-ray source and operating at 40 kV and 30 mA with an Ni filter. CA-PVC adduct was characterized by a Netzsch Differential Scanning Calorimeter 200 from 50° to 600°C using a flow rate of 20 mL/min and a heating rate of 10°C/min. The PVC obtained and the commercial PVC were analyzed using a thermogravimetric analyzer (TGA) DuPont 2950 from 50° to 600°C under a flow rate of 20 mL/min and a heating rate of 10°C/min. Gel permeation chromatography (GPC) was performed using a Waters GPC 600E unit with RI (Waters 410) and UV detectors (Water 486). The columns were HR 0.5, HR 4E, and HR 5E for the molecular weights $0\text{–}1 \times 10^3$, $0\text{–}1 \times 10^6$, and $5 \times 10^3\text{–}1 \times 10^6$, respectively.

RESULTS AND DISCUSSION

CA Guest Free

Tsutsumi et al. reported the successful inclusion polymerization of 1-chlorobutadiene by using the guest adsorption technique on guest-free crystal of deoxycholic acid to obtain poly(1-chlorobutadiene) with almost 100% of head-to-tail units for the trans-1,4-configuration[11]. Thus, this is one of the potential approaches to prepare CA-VCM adduct by the guest adsorption method. In the first step, guest-free CA for VCM inclusion was needed. Miyata et al. demonstrated the inclusion compound of CA and a series of vinyl monomers including methyl methacrylate (MMA)[12]. In the present work, the CA guest-free crystal was prepared from CA-MMA adduct by heating in vacuo overnight to exclude MMA. From the viewpoint of the size and structure of the MMA molecule, it can be expected that the channel remaining after MMA exclusion is appropriate for VCM.

Figure 1(a) shows the Fourier transform infrared (FT-IR) spectrum indicating the formation of CA-MMA inclusion compound, as referred to by the bands at 1699 cm^{-1}for carbonyl group, 1633 cm^{-1} for C=C stretching of MMA, and 1720 cm^{-1} for carbonyl group of CA. After guest exclusion, the FT-IR returns to the starting CA, as shown in Figure 1(b).

CA-VCM Inclusion Adduct

The guest-free CA crystals immersed in liquefied VCM at −15°C for three days show the bands at 1604 cm^{-1} for C=C stretching and at

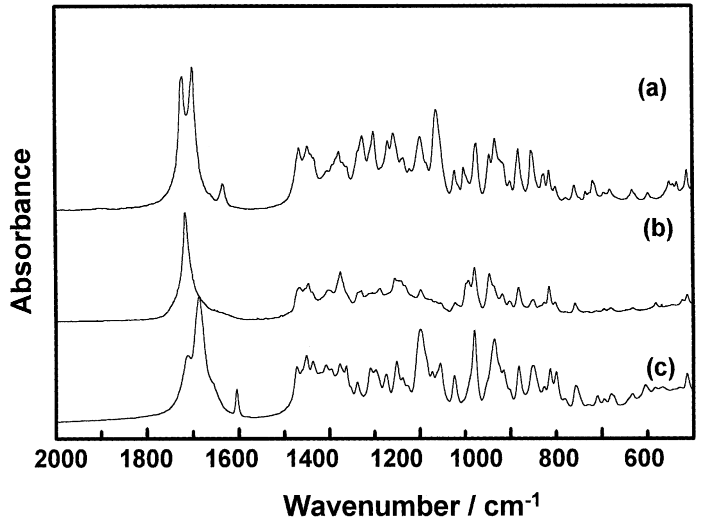

FIGURE 1 FT-IR spectra of (a) CA-MMA; (b) CA-MMA after guest exclusion; and (c) after immersing (b) in liquefied VCM for three days.

3084 cm^{-1} for C–H stretching of VCM, see Figure 1(c). This implies that the VCM adsorption into the CA channel occurred.

Low-temperature DSC was applied to clarify the stability of the CA-VCM adduct. Figure 2 shows that after VCM adsorption, CA gives a new endothermic broad peak in the range of 40°–50°C, Figure 2(b), as compared to the CA before VCM adsorption, Figure 2(a). It should be noted that the release temperature of VCM, at 40–50°C in Figure 2(b), is much higher than its own boiling point (−13°C) for over 50°C, implying the stability in the CA channel. The TGA studies also indicated that the VCM guest was released out of the CA channel starting at 40° with the weight loss about 11% (Figure 3). This percent weight loss was calculated for the host:guest molar ratio of CA:VCM and found to be 1:1. The XRD patterns changed gradually as compared to the CA guest free[13]; see Figures 4(a) and 4(b). A dramatic change of the pattern is observed after seven days; see Figure 4(c). This implies the successful incorporation of VCM guest in the CA channel and the change in packing structure after introducing VCM into the CA guest-free channel.

Inclusion Polymerization of CA-VCM Adducts

The adduct after irradiation was characterized to confirm the inclusion polymerization. The FT-IR of the CA-VCM adduct after γ-ray irradiation (Figure 5) demonstrates the bands at 611, 614, and 693 cm^{-1}, which

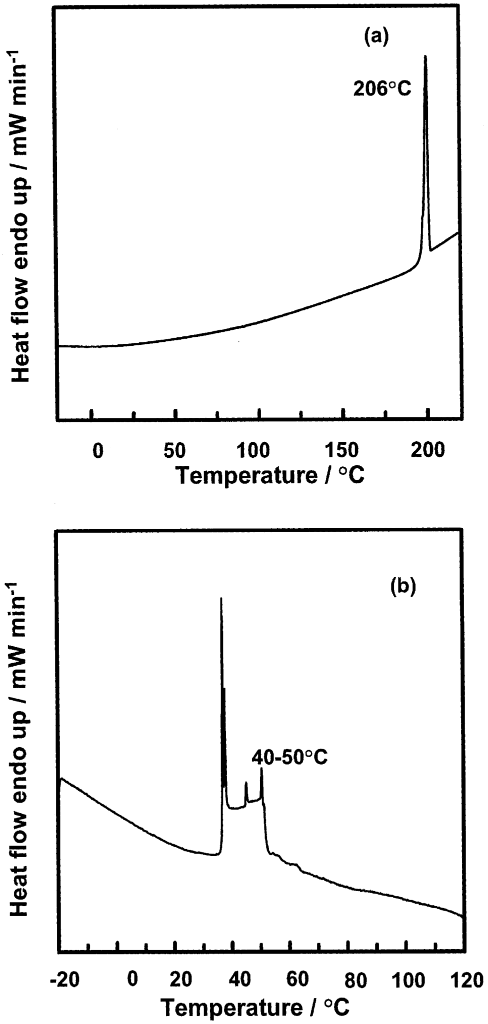

FIGURE 2 DSC thermograms of (a) CA guest free; and (b) CA guest free after VCM adsorption to become CA-VCM.

are assignable to C–Cl stretching of PVC, while some bands refer to the CA host. This suggests that VCM can be polymerized in CA to become PVC. In the other words, CA-VCM is changed to CA-PVC. The resulting adducts show three endothermic peaks in DSC (Figure 6). The peaks at 200° and 398°C refer to the melting point and decomposition of CA,

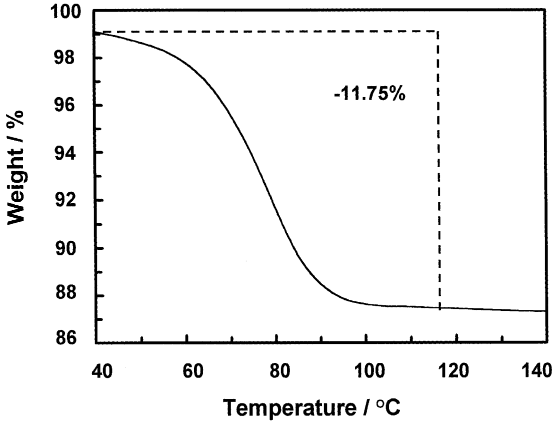

FIGURE 3 TGA thermogram of CA-VCM.

respectively. The inclusion PVC gives the broad degradation temperature from 220° to 355°C. Compared to commercial PVC, the degradation of PVC was found at 280°C. Thus, the broad peak suggests that PVC was generated in the CA host channel and implies that adsorption and inclusion polymerization of CA-VCM were successful.

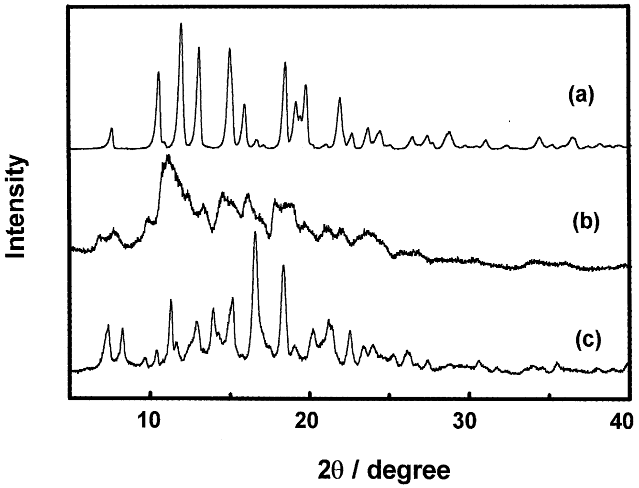

FIGURE 4 XRD patterns of (a) CA guest free; (b) CA after VCM adsorption for two days; and (c) CA after VCM adsorption for seven days.

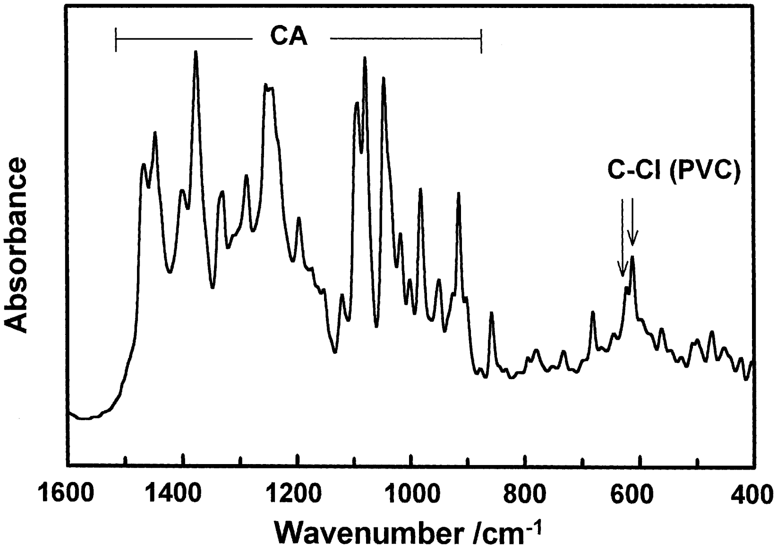

FIGURE 5 FT-IR spectrum of CA-VCM after radiation.

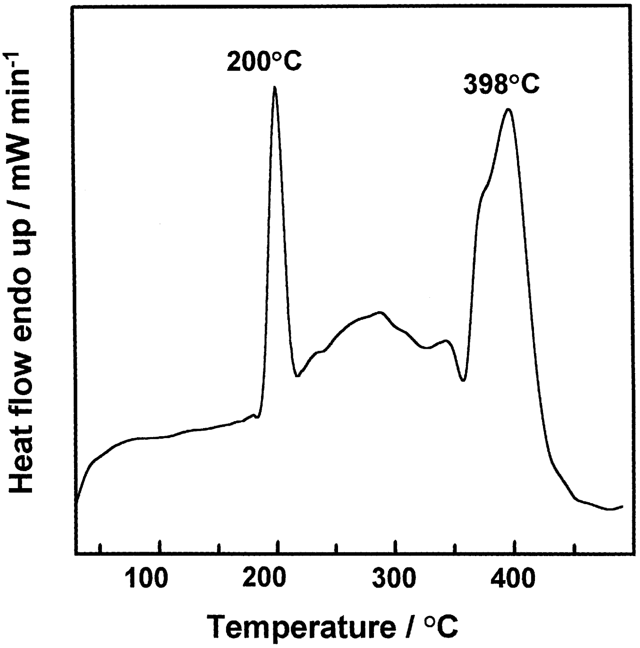

FIGURE 6 DSC thermogram of CA-VCM after radiation.

Structural Analysis of the obtained PVC

Figure 7(a) shows the FT-IR spectrum of the PVC obtained, as compared to that of the commercial PVC, Figure 7(b). It is known that in the case of PVC, the C–H stretching of syndiotactic and isotactic methylene species[14] can be observed at 1428 and 1434 cm^{-1}, while the C–Cl stretching for syndiotactic and isotactic species is at 640 and 690 cm^{-1}[15]. Curve-fitting techniques and quantitative FT-IR were applied to evaluate each PVC macrotacticity. Figure 8 summarizes the relative intensity of 640/2910 and 1428/2910 cm^{-1} (using the methylene peak at 2910 cm^{-1} as an internal standard). Although the tacticity was not significant, we found that the PVC obtained from CA-VCM was more syndiotactic rich than commercial PVC. The inclusion polymerization of VCM in CA channels might be controlled by the channel space where the molecules are preferable for syndiotactic structures when polymerization proceeds.

The stereoregularity was also investigated by ^{1}H-NMR. The peaks from 4 to 5 ppm are assigned to the proton of –CHCl–. The peaks from 2 to 2.5 ppm represent methylene protons of PVC backbone. Figure 9 shows the peaks splitting at 4.6, 4.5, and 4.4 ppm for triads belonging to rr, mr, and mm, respectively. In the case of inclusion PVC, Figure 9(a), the rr band is significant compared to that of commercial PVC, Figure 9(b). This result supports those from FT-IR, which shows significant

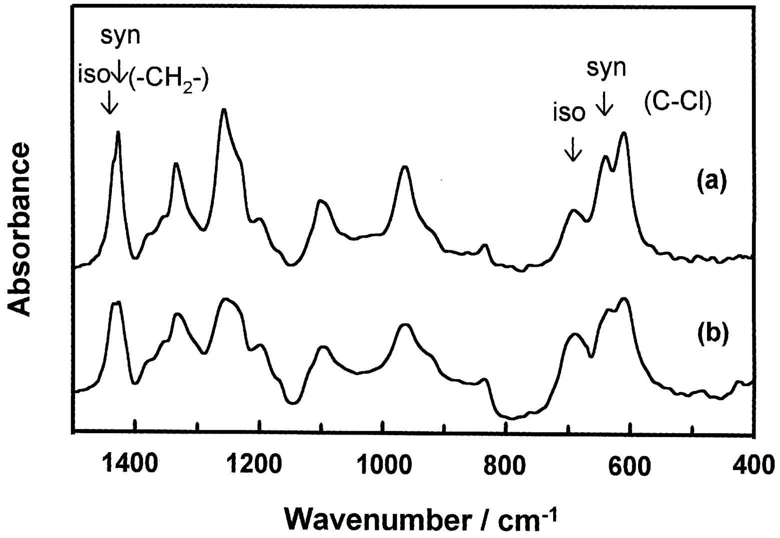

FIGURE 7 FT-IR spectra of (a) inclusion PVC; and (b) commercial PVC.

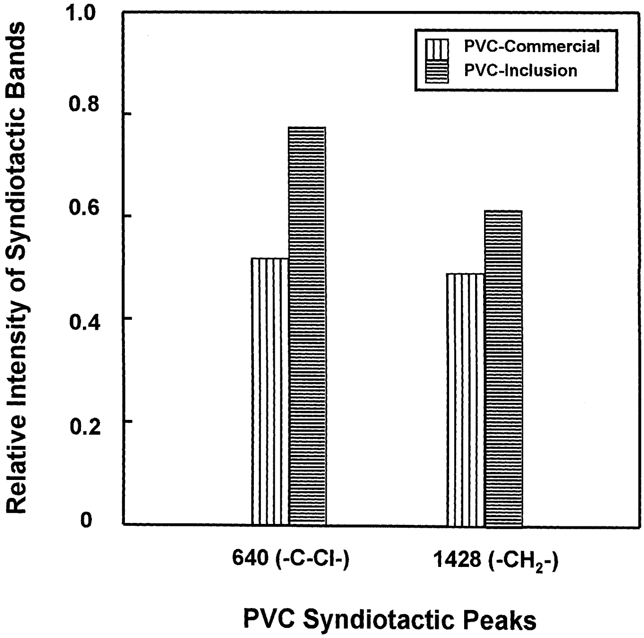

FIGURE 8 Relative syndiotacticity of commercial PVC, and inclusion PVC quantitatively analyzed by FT-IR using methylene stretching peak at 2910 cm^{-1} as an internal standard.

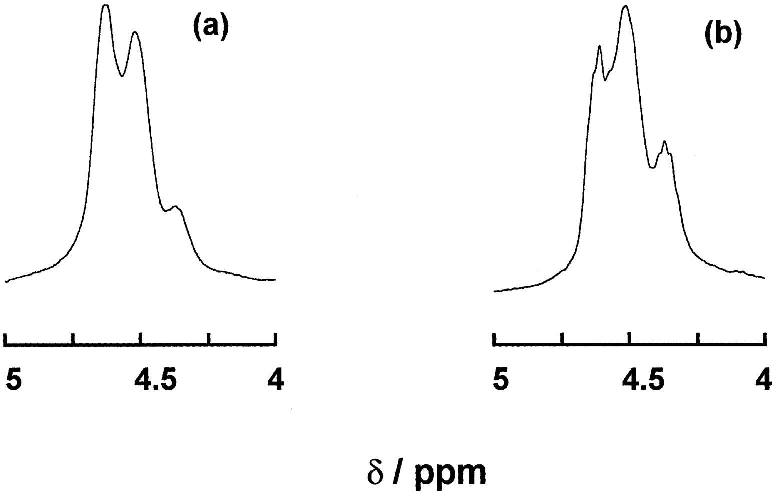

FIGURE 9 ^{1}H-NMR spectra of (a) inclusion PVC; and (b) commercial PVC.

TABLE I Percent microtacticity of each PVC quantitative analysis by ^{1}H-NMR using chemical shift 4.2–4.5 ppm

Sample	mm (%)	mr (%)	rr (%)
PVC inclusion	10	42	48
PVC commercial	24	48	28

syndiotacticity. The ratio of the integrated triad peaks were calculated to observe the microtacticity of each PVC. As shown in Table I, the inclusion-PVC gave rr and mr triads at a similar level for 40–50%, while the commercial PVC gave rr and mm for only 24–28%. This also supports the assumption that the PVC obtained is mainly a syndiotactic one.

The thermal stability studied by TGA showed that the commercial PVC gave the decomposition temperature from dehydrochlorination and chain degradation at 290°C while that of inclusion PVC was at 316°C.

Molecular Weight Characterization of the Obtained PVC

It should be noted that in most cases inclusion polymerization shows some limitation in obtaining high molecular weight. Miyata et al. reported CA derivatives, deoxycholic acid (DCA), to give inclusion polymerization of trans-1,3-pentadiene with molecular weight 3500 and of 1,3-chlorobutadiene with molecular weight 12,600[16,18]. Finter and Wegner studied inclusion polymerization of butadiene in tris(*o*-phenylenedioxy)cyclotriphosphazene host compound and reported a high molecular weight (3×10^5 g/mol) product[6]. In the case of inclusion PVC, although Minagawa et al. reported that the inclusion PVC from the urea channel gave syndiotactic polymer as determined from solid-state NMR, studies on molecular weight were not carried out[19]. The molecular weight of PVC obtained in the present article shows the molecular weight article at the level of 10^5 g/mol (Table II).

Effect Of γ-Ray

In general, γ-ray radiation induces the polymerization as well as the chain degradation. Figure 10 shows the molecular weight of PVC produced from CA-VCM when we varied the irradiation amount at the postpolymerization time for two days. Due to the limitation of our irradiation system, we started from 10 kGy and found that the molecular weight was about 4.35×10^5 g/mol. When the irradiation amount was

TABLE II Postpolymerization effects on PVC amount generated per CA-VCM adduct 1 g, molecular weight, and molecular weight distribution, at the irradiation dose 30 kGy

Postpolymerization time (days)	PVC amount generated per CA-VCM adduct 1 g (g)	$Mn \times 10^{-5}$	MWD
2	1.00	2.03	2.88
7	1.11	2.43	1.41
14	1.53	2.41	1.37
40	1.81	2.59	1.34

increased from 10 to 40 kGy, the molecular weight of the resulting polymer decreased gradually (Figure 10). This implies that at doses more than 10 kGy, a large amount of radical species might have been generated and lead to shorter polymer chains. Figure 10 also lists the PVC yield per 1 g of CA-VCM adduct. It is important to note that the amount of PVC

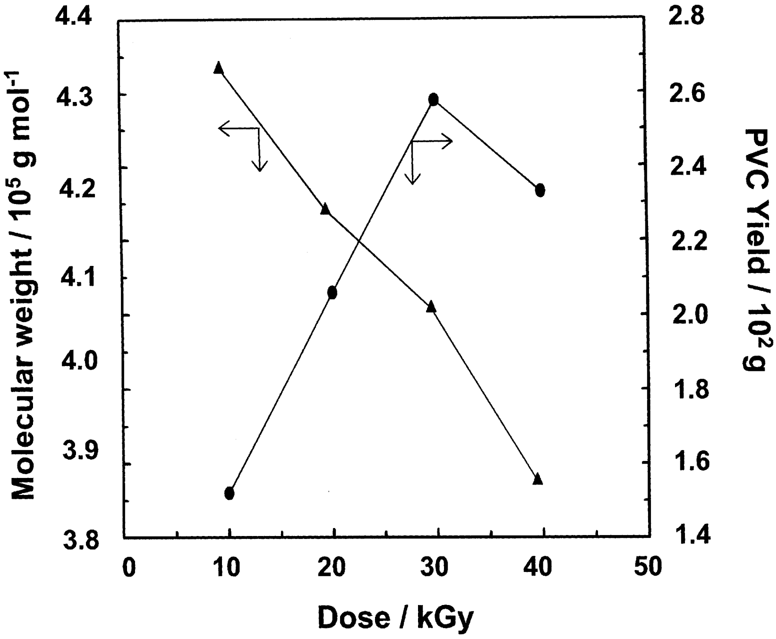

FIGURE 10 Molecular weight of the inclusion PVC and PVC yield calculated from CA-VCM adduct 1 g at various doses of irradiation.

obtained drastically decreased when the dose was increased to 40 kGy. This might be due to the high irradiation dose causing chain degradation. As evidenced in our procedure of dissolving the CA-PVC in methanol to collect PVC, we found an amount of white colloids dissolving in methanol while washing the PVC. The dissolved portions might be the degraded species.

Effect of Postpolymerization Time

In most cases of inclusion polymerization, the living radicals proceed to polymerize for days. Table II shows the effect of postpolymerization time at the irradiation of 30 kGy. The amount of PVC at 14–40 days is 1.5–1.8 times to that at 2 days. In all cases, the molecular weight obtained is in the range of $2.4\text{–}2.6 \times 10^5$ g/mol. The reason that postpolymerization time gave little effect on the molecular weight might be because the host cavity limits the movement of the radicals along the channel after a certain polymer chain length is produced.

CONCLUSIONS

Vinyl chloride monomer (VCM) was successfully introduced in cholic acid (CA) guest-free crystal by using the guest adsorption process. VCM was stabilized in the CA channel as observed from the changing of XRD patterns, guest releasing peaks in DSC, and the peaks in FT-IR. The inclusion polymerization gave PVC with molecular weight at the level of 10^5 g/mol as confirmed by FT-IR, NMR, and GPC. The postpolymerization time exhibited little effect on the molecular weight of inclusion PVC. Tacticity studies implied that the CA channel provided syndiotactic-rich PVC.

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