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ORIGINAL PAPER

Thermally decomposable phosphonate ester polymer gels

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Abstract A polymerizable dimethacryloyl vinylphosphonate (DMVP) was developed as a novel crosslinking agent by esterification of vinylphosphonic acid and methacryloyl chloride in the presence of triethylamine. Then, poly(DMVP) (PDMVP) was generated by bulk polymerization solution at 30, 45, and 80 °C in the presence of a radical initiator. The resultant PDMVP, polymerized at 45 and 80 °C, could be dissolved in acetone, water, and *N*-methylpyrrolidone. However, PDMVP obtained at 30 °C showed to be insoluble in such solvents and became a gel instead. It was found that the formed gel was soluble when heating due to hydrolysis of the ester bonds in the polymer. Evidence was presented showing the thermal decomposition behavior of the PDMVP gel, which showed an irreversible solid-to-liquid phase transition.

Keywords Thermal decomposition · Phosphonate · Crosslinking agent · Gel

Introduction

As commonly known, bi- or tri-functional crosslinkers in radical polymerization are necessary to prepare functional crosslinked polymers. In order to obtain certain features such as thermal stability, hardness, insolubility, molecular recognition ability, and so on [1–5], many kinds of crosslinking monomers for radical polymerization have been widely used including divinylbenzene, *N*,*N*′-methylene-*bis*-acrylamide and ethyleneglycol diacrylate. We have noted that polymerizable monomers having phosphonic acid groups would have an advantage for the synthesis of phosphonic acid polymers such as poly(vinylphosphonic acid) (PVPA),

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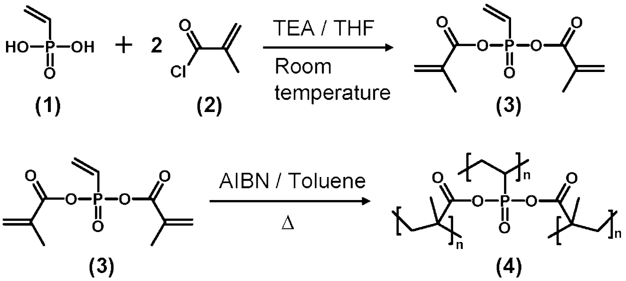
poly(vinyl diethyl phosphonate), and diisopropyl-*p*-vinylbenzyl phosphonate [6, 7]. Since PVPA shows high water solubility, biocompatibility, and high incombustibility, a crosslinked PVPA is expected to be potentially useful for various applications such as adhesion promoters in dental cements, dopants in conductive blends, and flame retardants [8–14]. For these reasons, a novel crosslinked phosphonate polymer obtained from polymerizing dimethacryloyl vinylphosphonate (DMVP) becomes a promising material. In this study, we aimed to synthesize a novel crosslinking agent containing phosphonate groups by radical polymerization and investigate the properties of the resultant crosslinked polymers. So far, there were several reports for esterification of phosphonic acid; especially, a way of condensing between phosphonic acid and alcohol has been well known [15]. Also, the formation of phosphonate from trialkyl phosphite and alkyl halide has been reported [16]. However, very few reports on the reactions of phosphonic acid and acyl compounds such as carboxylic acid, aldehyde, and carboxylic halide can be found and are as follows: Püdovik et al. [17] discovered that the reaction of dimethyl methylphosphonate and acetyl chloride could generate a mixture of dimethyl methylpyrophosphonate and acetic acid anhydride via methylacetyl methylphosphonate as an intermediate. Recently, Millaruelo et al. [18] described that reaction of VPA and acetic acid anhydride produced a mixture of di-acetylated VPA, mono-acetylated VPA, and others. However, the details of such reaction are still not well known. Also, Opper et al. [19] designed a polyethylene containing diethyl phosphonate segments. Then, phosphonate segments on the polyethylene backbone were hydrolyzed by using trimethylsilyl bromide in methanol. Moreover, Watanabe [20] reported the thermal decomposition of sodium cycro-hexaphosphate hexahydrate, which gave sodium cycro-triphosphate at about 450 °C by passing through an anhydrous sodium cycro-hexaphosphate phase.

On the basis of the background for esterification of phosphonic acid, in this study, DMVP was synthesized by the reaction of VPA and methacryloyl chloride (MC) with *tri*-ethylamine (Et_3N). Then, the resultant monomer was polymerized by radical polymerization in order to obtain poly(dimethacryloyl vinylphosphonate) (PDMVP) (Scheme 1). The Resultant PDMVP might be expected to hydrolyse by catalyst and heat energy, since PDMVP contains unstable bonds of phosphonate group, which shows decomposition depending on temperature [21–24]. Here, we



Scheme 1 Synthesis of DMVP (3) by esterification of VPA (1) and MC (2). PDMVP (4) was prepared by radical polymerization of DMVP

examined the thermal degradation property of PDMVP obtained by radical polymerization of the DMVP monomer. Then, the thermal decomposition behavior of the PDMVP was characterized to demonstrate as novel thermally decomposable crosslinked polymers.

Experimental

Monomer synthesis and polymerization

DMVP was synthesized by esterification of vinylphosphonic acid (VPA) and MC in the presence of triethylamine (TEA). Both TEA (277.8 mmol) and MC (185.2 mmol) were added dropwise into a tetrahydrofuran (THF) solution containing VPA (46.3 mmol) at 0 °C. After keeping at room temperature for 24 h, the precipitated mixture was filtrated in order to remove TEA salts and then the solvent was evaporated. The obtained DMVP was washed five times with water and the insoluble part was passed through a silica column in order to remove the unreacted VPA and acrylic acid. Then, the obtained DMVP was characterized by FT-IR spectroscopy (Shimadzu, IR-prestage 21), differential scanning calorimetry (DSC) (Rigaku, Thermo plus EVO), ^{1}H NMR and ^{31}P NMR spectroscopy (JEOL, JNM-AL400). The ^{1}H NMR and ^{31}P NMR spectra were referenced on internal tetramethylsilane ($\delta(^{1}\mathrm{H})=0$ ppm) and external trimethyl phosphite ($\delta(^{31}\mathrm{P})=$ 140 ppm), respectively. The DSC measurements were carried out for DMVP (12 mg) in the range of 25 and 200 °C with a heating rate of 5 °C/min in the air. FT-IR, ^{1}H NMR, ^{31}P NMR, and DSC data of DMVP were obtained as follows: IR (KBr): C=O stretching band at 1755 cm^{-1}, P–O–C stretching band at 1035 cm^{-1} and no O–H stretching band at around 3500 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, δ ppm): 1.95 (s, 6H, CH_3), 5.86–6.31 (d, 4H, $=CH_2$), 5.60–6.66 (m, 3H, $-CH=CH_2$). ^{31}P NMR (161.5 MHz, $CDCl_3$, δ ppm): 131.65. DSC (ΔH J/g): −10.7 (130 °C), 2.3 (148 °C), and −2.3 (168 °C).

In order to obtain the homopolymer, radical polymerization was performed by the following procedure: DMVP (15 g) and AIBN (1.5 g) were dissolved into toluene (5 g). Then, the free radical polymerization was carried out at 30, 45, and 80 °C for 24 h in an erlenmeyer flask after N_2 bubbling for 1 h. As a result of polymerization, PDMVP was obtained at 30 °C (PDMVP30), 45 °C (PDMVP45), and 80 °C PDMVP80. The crosslinked PDMVPs were washed and swelled with acetone to remove unpolymerized monomers and then dried in vacuo. The obtained PDMVPs were characterized by FT-IR spectroscopy with KBr method. The yields obtained for PDMVP30, PDMVP45, and PDMVP80 were 39.4, 36.4, and 18.4%, respectively.

Measurements of thermal and mechanical properties of PDMVP

Properties of dried PDMVPs were investigated by DSC (Rigaku, Thermo plus EVO), Rheometer (Anton Paar, Rheoplus), and in situ FT-IR spectroscopy (Shimadzu, IR-prestage 21) at different temperatures. In the DSC measurements for

PDMVPs (12 mg), the data were obtained in the range of 25 and 200 °C with a heating rate of 5 °C/min in the air. In the viscoelastic measurement, the values of storage and loss elastic modulus of the gels were measured at different frequencies. The viscoelasticity of PDMVP swelled with acetone was evaluated in the range of 1×10^{-3} and 1×10^{2} Hz at 25 °C. Herein, the thickness of each PDMVP was arranged to about 1 mm. In order to compare the viscoelasticity and solvent uptake of the PDMVP30 with and without heating, dried PDMVP30 was heated at 180 °C for 10 min in the air. Then, the resultant PDMVP180 was similarly used for viscoelasticity and subsequent solvent uptake measurements. In situ FT-IR spectra measurements for dried PDMVP30 carried out in the range of 20 and 190 °C. The dried powder samples were pinched with two CaF_2 glasses (32 mm diameter with 3 mm thickness) and then set in a holder (ST. Japan Inc., HT-32) in order to heat them to the programed temperature using a controller (ST Japan Inc., TXN-700-B). While the sample heating at a rate of 5 °C/min was carried out in the air, FT-IR spectra were simultaneously measured with in situ observation in the range from 20 to 190 °C.

The apparent values of solvent uptakes for PDMVPs were also measured as the crosslinked polymer characteristics in the following manner: vacuum-dried PDMVP (0.05 g) with dry weight, w_{dry}, was immersed in acetone, water, toluene, and *N*-methylpyrrolidone (NMP). The sufficiently swelled polymers for 3 days at room temperature were filtrated and then weighed. The equation of solvent uptakes for PDMVP was calculated as follows

$$\text{Solvent uptake } [\%] = \frac{w_{\mathrm{swell}} - w_{\mathrm{dry}}}{w_{\mathrm{dry}}} \times 100$$

For examining the heating effect on the gel sample, PDMVP30 gels swelled with NMP ($20 \times 20 \times 3$ mm^3) were put into NMP solution and then heated at 5 °C/min on a hot plate from 20 °C to 130 °C.

Results and discussion

In this study, DMVP monomer as a novel crosslinking agent was synthesized according to Scheme 1 by esterification of VPA and MC. The resultant monomer, a brown color liquid, 67.9% in yield, was soluble in various organic solvents such as toluene, acetone, THF, ethanol, NMP, and chloroform and insoluble in water and diethylether. DMVP homopolymers were prepared in toluene by radical polymerization of the obtained DMVP monomer at 30, 45, and 80 °C. The characteristics of the resultant PDMVP were confirmed by using FT-IR spectroscopy by KBr method. As shown in Fig. 1c, C=O stretching bands at 1805 and 1740 cm^{-1}, PO–C stretching band at 1030 cm^{-1}, and no O–H stretching bands were observed near 3500 cm^{-1}. As seen from the FT-IR spectra of PDMVP80 (Fig. 1a), the O–H stretching band at around 3500 cm^{-1} was clearly observed. This suggested that a part of PDMVP was hydrolyzed into phosphonic acid and carboxylic acid segments by heating during the polymerization. Then, their respective IR peaks in the case of OH groups became weaker depending on the polymerization temperature. This

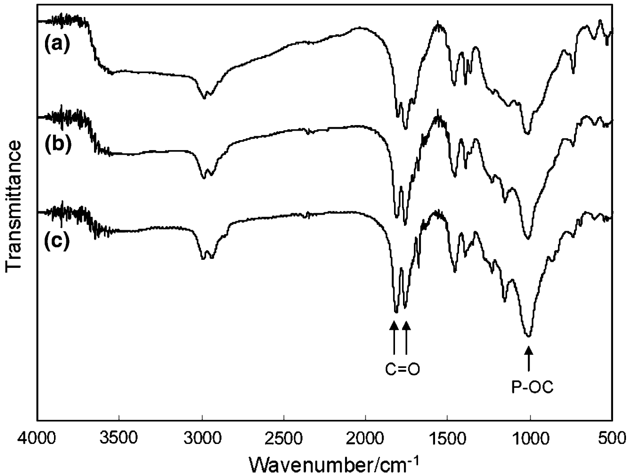


Fig. 1 FT-IR spectra of *a* PDMVP80, *b* PDMVP45, and *c* PDMVP30

meant that the hydrolytic decomposition of the PDMVP was not happened at lower temperatures in the polymerization process. Therefore, the polymerization yields might be increased at lower polymerization temperatures.

Figure 2 shows DSC curves for three PDMVPs. It was noted that thermal degradation peaks were widely seen in the range of 105 and 185 °C for the PDMVP30 (Fig. 2c). However, such peak was significantly decreased and narrowed

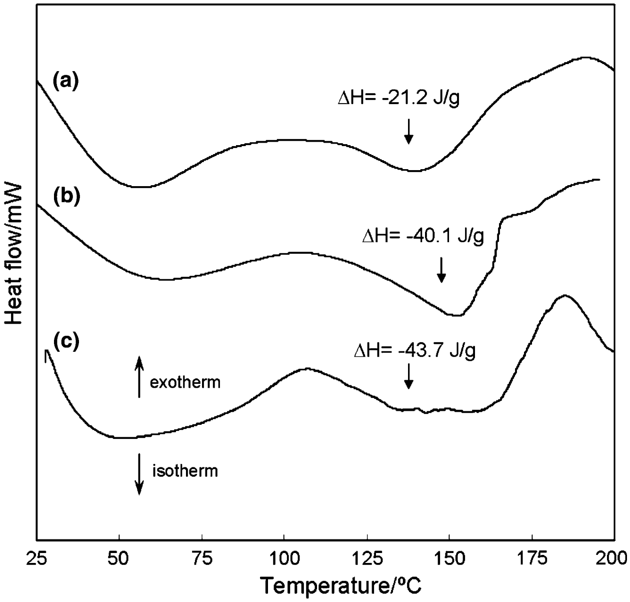


Fig. 2 DSC curves of *a* PDMVP80, *b* PDMVP45, and *c* PDMVP30

on DSC curves of PDMVP80. From the endotherm peaks, the thermodynamic values of ΔH were −43.7, −40.1, and −21.2 J/g for PDMVP30, PDMVP45, and PDMVP80, respectively. These tendencies suggested that most of DMVP segments in the PDMVP80 were already decomposed during polymerization and the PDMVP30 kept much DMVP segments.

Although it was impossible to estimate precise value of solvent uptakes to the gels, examining such property of the obtained PDMVPs was meaningful. Thus, apparent values of solvent uptakes were investigated using toluene, water, acetone, and NMP. As shown in Table 1, PDMVP30 could absorb all of toluene, acetone, water, and NMP. The apparent values of the solvent uptakes were progressively large in NMP for 350% and others were acetone 33%, water 23%, toluene 10%. For the PDMVP45, PDMVP80, and PDMVP180, toluene uptake was hardly observed. This meant that their crosslinked gels were partially dissolved into acetone and water, but non-soluble parts in such solvent still remained in the gel matrix. When we observed similarly in the PDMVP45, PDMVP80, and PDMVP180, the NMP solvent completely dissolved. These tendencies demonstrated that three-dimensional networks in the PDMVP gels were broken by heating.

Then, the viscoelasticity changes by thermal degradation were measured at 25 °C for the PDMVPs swelled with acetone. This is because the viscoelasticity data were important for understanding the properties of the crosslinked gels. Figure 3 shows the storage elastic modulus, G', and the loss elastic modulus, G'', at different frequencies. It was cleared that the values of G' showed the plateau region with no depending on frequency and those of G'' significantly increased at high frequency for all PDMVP gels. It was observed that PDMVP30 had 3.2×10^3 Pa of G' and 5.0×10^2 Pa of G'', whereas the PDMVP80 displayed 5.5×10^2 Pa of G' and 9.5×10^1 Pa of G''. These data suggested that viscoelasticity values of the PDMVP30 gel were higher than those of the non-dissolved parts of the PDMVP80. Therefore, this tendency indicated that the PDMVP80 showed lower crosslinking, whereas the PDMVP30 retained their highly crosslinking parts. As suggested, the values of G' and G'' of 2.8×10^1 and 2.8 Pa for PDMVP180 were two orders lower than those of the PDMVP30. This meant that the crosslinkage bonding of the ester part was easily decomposed at higher temperatures. Figure 4 shows pictures of the swelled PDMVP30 gel in NMP solution at various temperatures. The data clearly

Table 1 Solvent uptakes of PDMVPs for various solvents

	Solvent uptake ($g_{\text{solvent}}/g_{\text{polymer}} \times 100\%$)			
	Toluene	Water	Acetone	NMP
PDMVP30	10 (2.0)	23 (4.0)	33 (2.0)	350 (50)
PDMVP45	1.8 (0.1)	P	P	C
PDMVP80	1.4 (0.1)	P	P	C
PDMVP180	1.1 (0.3)	P	P	C

P and C stand for partially dissolved and completely dissolved, respectively

Standard deviation σ expressed in parenthesis

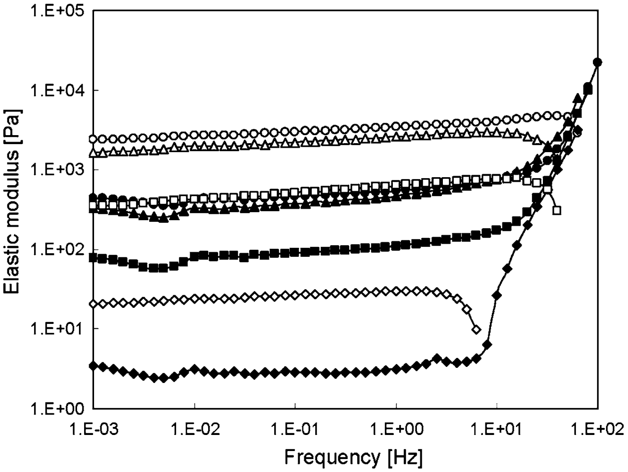


Fig. 3 Viscoelastic behaviors of PDMVPs swelled with acetone. *Open and filled circles* are the storage (G') and loss elastic modulus (G'') of PDMVP30. *Open and filled triangles* are the storage and loss elastic modulus of PDMVP45. *Open and filled squares* are the storage and loss elastic modulus of PDMVP80. *Open and filled diamonds* are the storage and loss elastic modulus of PDMVP180

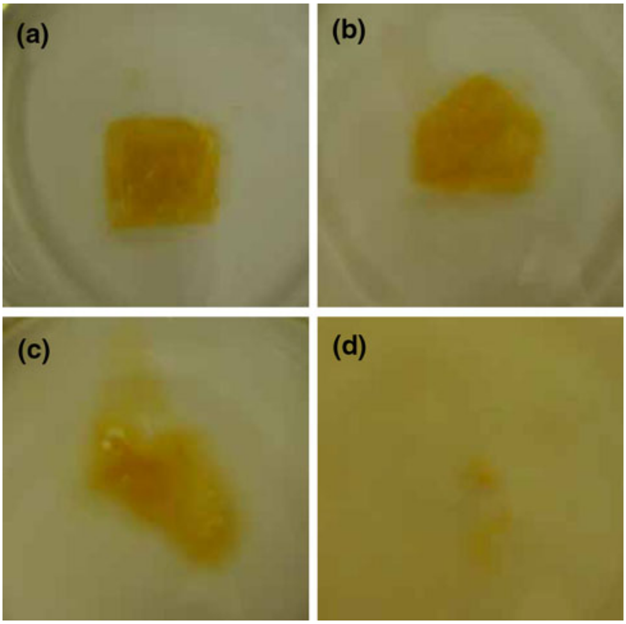


Fig. 4 Pictures of PDMVP30 gel in NMP solution at **a** 20 °C, **b** 80 °C, **c** 105 °C, and **d** after holding at 130 °C for 30 min

showed that the swelled PDMVP30 was dissolved over 105 °C. After the solution temperature was kept at 130 °C for 30 min, it was completely dissolved into the NMP solution. Then, the gelatinous solid was no found after the temperature

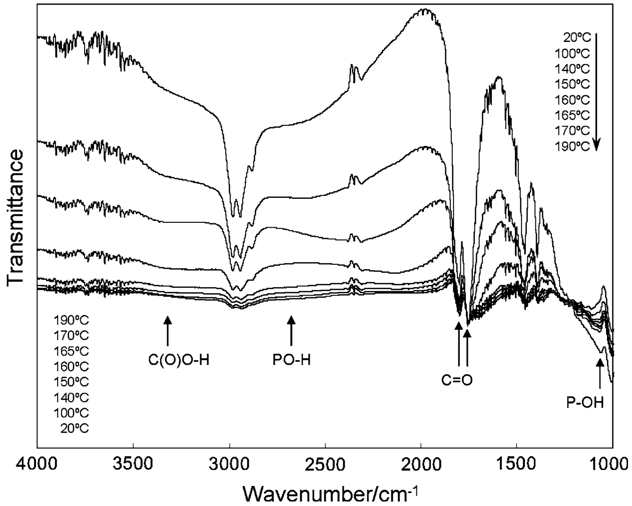


Fig. 5 In situ FT-IR spectra of PDMVP30 with increasing temperature

returned to 20 °C. This tendency indicated that the crosslinking of the PDMVP30 was irreversible. Thus, this strongly supported that the thermal decomposition of crosslinking was observed at 105 °C.

Figure 5 shows in situ FT-IR spectra of dried PDMVP 30 observed in the range 20 and 190 °C. When the temperature increased from 20 to 100 °C, significant spectral changes were not seen. After 100 °C was passed, the baseline transmittance gradually increased. This was due to that solid PDMVP30 powders were gradually melted inside the CaF_2 windows and then the sample became transparent. As the temperature was increased, the intensity of peaks of C=O bands appeared in 1760 and 1800 cm^{-1} changed. This might indicate that phosphonate ester bonds were hydrolyzed to both COOH and POH groups. Actually, the P–OH stretching band at 1080 cm^{-1} gradually appeared by increasing the temperature. Also, the O–H stretching band in the range 2500 and 3300 cm^{-1} was observed with broaden peak. These spectral data demonstrated that the bonds of the phosphonate ester were broken by increasing the temperature. Therefore, the gel behavior of the resultant pictures in Fig. 4 was caused by decreasing a number of crosslinkage of phosphonate ester bonds at higher temperature.

In conclusion, novel phosphonate ester crosslinking monomers and its crosslinked polymer were synthesized. The phosphonate ester groups (>C(=O)–O–P(=O)–O–C(=O)<) in the PDMVP could be hydrolyzed by heating over 105 °C and the reaction generated both COOH and $P(=O)(OH)_2$ groups from ester cleavage and then the gelatinous polymer was irreversibly melted. It is promised that such characteristics of PDMVP are useful in the field of adhesive promoter and other applications. And the thermally decomposable gels can strongly contribute such engineering field.

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