

## Radical Polymerization of 'Dehydroaspirin' with a Formation of Hemiacetal Ester Skeleton: A Hint for Recyclable Vinyl Polymers

Akane Kazama<sup>a</sup> and Yasuhiro Kohsaka<sup>\*a,b</sup>Received 00th January 20xx,  
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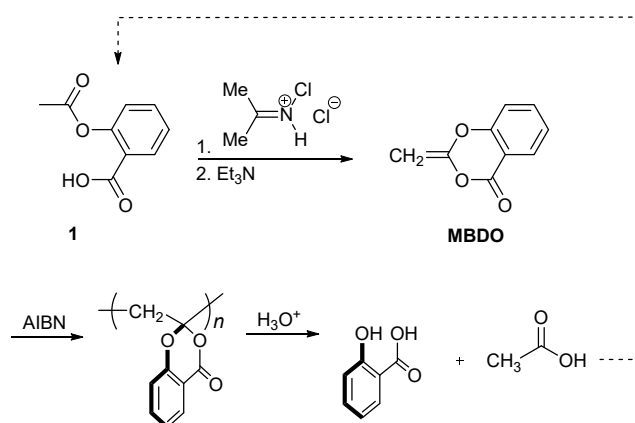
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A vinyl polymer with a cyclic hemiacetal ester skeleton was synthesized via the radical polymerization of 2-methylene-4H-benzo[d][1,3]dioxin-4-one (MBDO; so-called 'dehydroaspirin'). This material could be decomposed to acetic acid and salicylic acid (the raw ingredients for MBDO) by acid hydrolysis, and thus has potential as a recyclable vinyl polymer.

Plastics based on petrochemicals are currently an important aspect of modern society. However, due to the finite nature of petrochemical resources, there is significant interest in the development of polymers obtained from sustainable systems. There are two strategies for sustainable polymers: bio-based polymers that do not require petrochemicals<sup>1–8</sup> and recyclable polymers. A number of bio-based polymers are presently available, including polyesters,<sup>9–12</sup> polyamides<sup>13,14</sup> and polyurethanes,<sup>15</sup> and high-performance bio-based polymers have also been developed.<sup>16–19</sup> The second approach, involving recyclable materials, employs polymers that can be depolymerized to the corresponding monomers or their precursors such that they can be reused.<sup>11,20–23</sup> Many research projects have examined the recycling of common polycondensation polymers, such as polyethylene terephthalate<sup>24–27</sup> and polycarbonate.<sup>28–30</sup> In contrast, recyclable vinyl polymers have not yet been demonstrated, even though vinyl polymers are used much more widely than polycondensation polymers.

Recently, our group has focused on the polymerization chemistry of  $\alpha$ -functionalized acrylates,<sup>31–34</sup> which produce polymers that exhibit excellent degradability.<sup>34</sup> As an example, a cyclic acrylate (*i.e.* an exo-methylene lactone) with hemiacetal ester linkages was found to undergo either radical or anionic

polymerization to afford the corresponding vinyl polymer, which was subsequently converted to a water-soluble version via hydrolysis of the hemiacetal ester groups.<sup>32</sup> We are also interested in the analogous monomer 2-methylene-4H-benzo[d][1,3]dioxin-4-one (MBDO), which does not carry a hemiacetal ester moiety but can produce such groups through radical polymerization. In our initial plan, we had expected the acid hydrolysis of the resulting polymer should afford a polyketone with 1,3-dicarbonyl skeletons. However, remarkably, the polymer was found to be decomposed to acetic acid and salicylic acid, the raw materials for the synthesis of MBDO.



Scheme 1. Synthesis, polymerization and renewal of MBDO.

MBDO is sometimes referred to as 'dehydroaspirin,' because it affords acetylsalicylic acid (aspirin) upon the addition of water.<sup>35</sup> In the present work, MBDO was prepared from aspirin via two steps in conjunction with a moderate yield (72.9%, **Scheme 1**). The bulk radical polymerization of MBDO was conducted using 2,2'-azoisobutyronitrile (AIBN) as the initiator at 65 °C for 18 h (**Table 1**, Entry 1). The product was found to be largely insoluble in common organic solvents such as CHCl<sub>3</sub>, tetrahydrofuran (THF) and dimethylsulfoxide (DMSO), but CHCl<sub>3</sub> dissolved 36.0% by weight of the polymer and this

<sup>a</sup> Faculty of Textile Science and Technology, Shinshu University, 3-15-1 Tokida, Ueda, Nagano 386-8567, Japan. E-mail: kohsaka@shinshu-u.ac.jp; Tel: +81-268-21-5488

<sup>b</sup> Research Initiative for Supra-Materials (RISM), Shinshu University

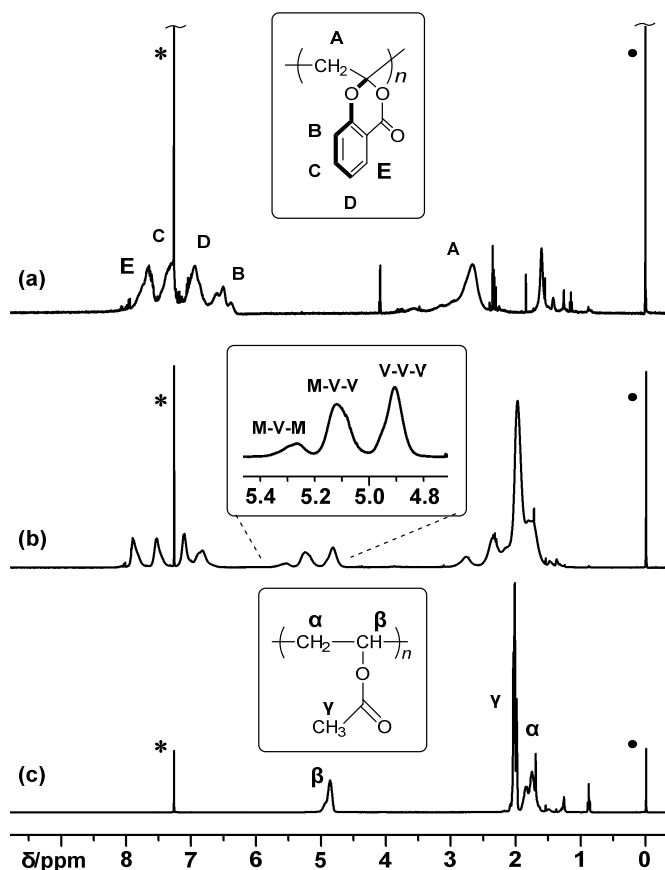
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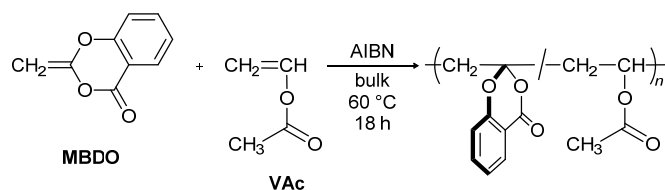
**Table 1.** (Co)polymerization of MBDO with VAc initiated by AIBN at 60 °C for 18 h in bulk.

Entry <sup>a</sup>	Feed		Conversion <sup>b</sup> [%]		Yield <sup>c</sup> [%]	Composition <sup>b</sup> [%]		$M_n^d$	$\mathcal{D}^d$	$T_d^e$ [°C]	$T_g^f$ [°C]
	MBDO	VAc	MBDO	VAc		MBDO	VAc				
1 <sup>g</sup>	100	0	99	-	(38.8) <sup>h</sup>	100	-	(2400) <sup>i</sup>	(2.10) <sup>i</sup>	(232) <sup>h</sup>	(132) <sup>h</sup>
2	75	25	87	68	> 99.9	89	11	24200	1.40		
3	50	50	88	64	69.5	61	39	37500	2.35	240	84
4	25	75	85	64	46.0	31	69	21600	1.73		
5	0	100	-	87	78.0	-	100	51200	4.67		32 <sup>j</sup>

<sup>a</sup> [Monomer]<sub>0</sub> / [AIBN]<sub>0</sub> = 1 / 0.02. <sup>b</sup> Determined by <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 26 °C). <sup>c</sup> (Yield) = (Polymer Weight)/(Monomer Weight) × 100%. <sup>d</sup> Determined by SEC (THF, 40 °C, polystyrene standards). <sup>e</sup> Determined by TG/DTA. <sup>f</sup> Determined by DSC. <sup>g</sup> Polymerized at 65 °C. <sup>h</sup> CHCl<sub>3</sub>-soluble fraction. <sup>i</sup> THF-soluble fraction. <sup>j</sup> Refer to ref. 45.

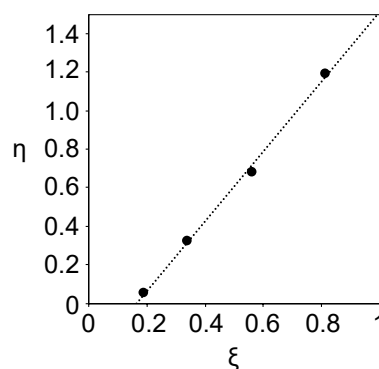


**Figure 1.** <sup>1</sup>H NMR spectra of (a) poly(MBDO), (b) poly(MBDO-co-VAc) (Entry 4 of Table 1) and (c) poly(VAc) (400 MHz, CDCl<sub>3</sub>, 25 °C). \*: CHCl<sub>3</sub> and •: Me<sub>4</sub>Si.



**Scheme 2.** Copolymerization of MBDO and VAc.

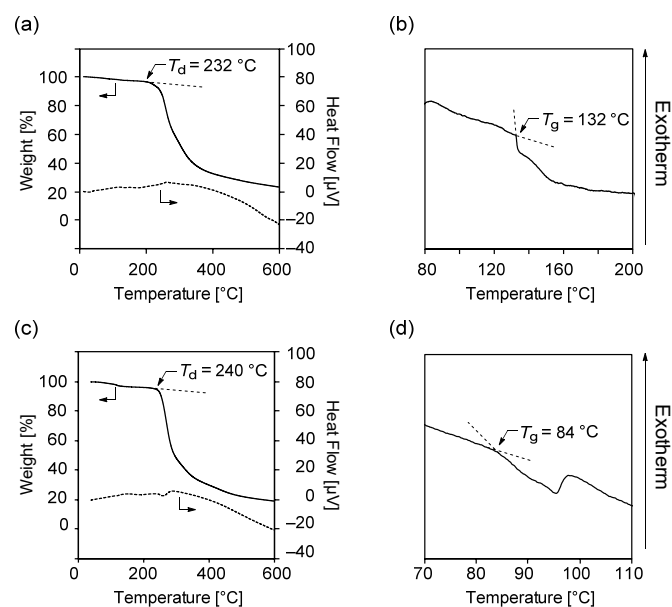
fraction was extracted. The <sup>1</sup>H NMR spectrum of this fraction [Figure 1(a)] exhibited aromatic signals in the range of 8.2–6.2 ppm and methylene signals in the range of 3.8–2.0 ppm, with the relative intensities expected for the vinyl polymer. The <sup>13</sup>C NMR spectrum (Figure S1) also confirmed the synthesis of the vinyl polymer. The infrared (IR) spectrum of the CHCl<sub>3</sub>-insoluble fraction was similar to that of the soluble material (Figure S2).



**Figure 2.** Kelen-Tüdös plots for the copolymerization of MBDO and VAc.

Therefore, the different solubilities of these two fractions are attributed simply to variations in molecular weight. The fraction extracted with CHCl<sub>3</sub> was re-dissolved in THF and its number average molecular weight and polydispersity were determined to be  $M_n = 2400$  and  $\mathcal{D} = 2.10$ , respectively.

The rigid polymer chains resulting from the packing of aromatic rings are believed to be responsible for the poor solubility of this material. To improve solubility to allow the entire polymeric structure to be assessed using NMR spectrometry, copolymerization with vinyl acetate (VAc) was conducted at various feed ratios (Scheme 2; Table 2, Entries 2–5, Figure S3 and Figure S4). All trials resulted in polymers with high molecular weights ( $M_n > 20,000$ ) and good solubility in common organic solvents such as CHCl<sub>3</sub> and THF. The <sup>1</sup>H NMR spectrum of one such copolymer [Entry 4, Figure 1(b)] was not a simple combination of the spectrum of each homopolymer [Figure 1(a) and (c)], but rather exhibited signals that could be assigned to each monomeric unit. This result suggested that the MBDO underwent vinyl polymerization without any side reactions. The composition of the copolymer was determined from the ratio of the intensity of the aromatic signals due to the MBDO units to the intensity of the methine signals due to the VAc units. As an example, the proportion of MBDO units in the polymer associated with Entry 4 in Table 1 was 31%. Notably, three methine proton signals resulting from the VAc units were observed over the range of 5.4–4.8 ppm, indicating the existence of three different triads: MBDO-VAc-MBDO (M-V-M), M-V-V and V-V-V. These data provided further confirmation that copolymerization had occurred. The relative reactivity of MBDO ( $M_1$ ) and VAc ( $M_2$ ) were determined by Kelen-Tüdös method from the polymerization in toluene (Figure 2, Table S1)<sup>36</sup> as follows:  $r_1 = 1.51$  and  $r_2 = 0.587$ . Therefore, MBDO has higher reactivity than VAc.

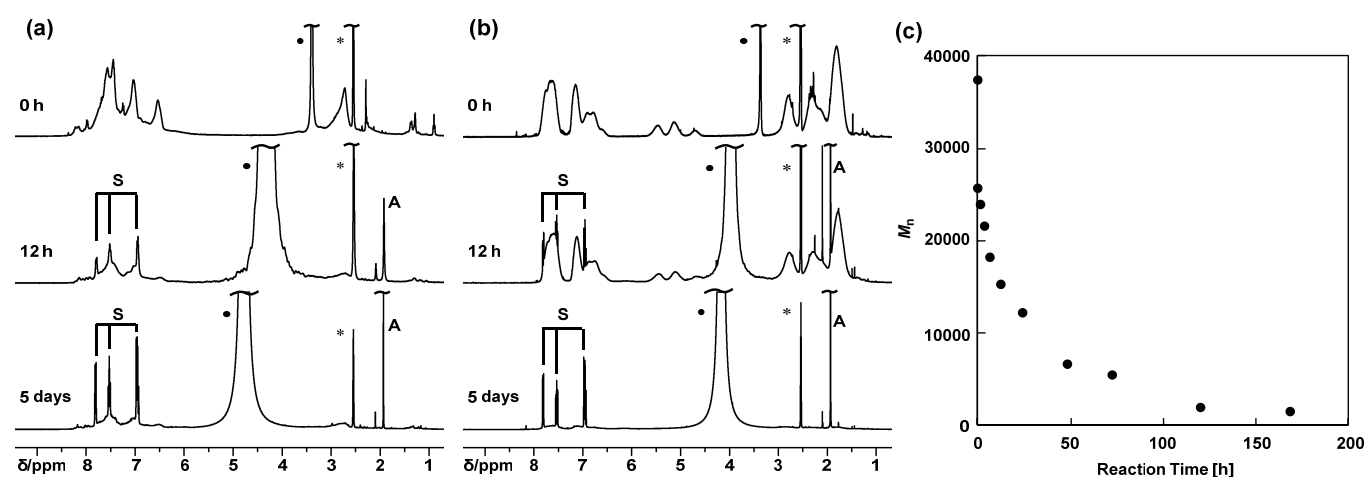


**Figure 3.** TG-DTA curves of (a) poly(MBDO) (Entry 1) and (b) poly(MBDO-VAc) (Entry 3) and DSC curves of (c) poly(MBDO) (Entry 1) and (d) poly(MBDO-VAc), respectively.

The vinyl polymerization of MBDO generates a hemiacetal ester skeleton that can be cleaved by heat<sup>37–40</sup> and Brønsted<sup>32</sup> or Lewis<sup>41</sup> acids. However, the DTA curve acquired from poly(MBDO) did not exhibit any peaks [Figure 3(a)], prior to the onset of mass loss ( $T_d$ ) at 232 °C, while the glass transition temperature ( $T_g$ ) was observed at 132 °C in DSC curve [Figure 3(b)]. The copolymer obtained in Entry 3 also exhibited no peaks in DTA curve below the  $T_d$  at 240 °C, while the  $T_g$  was determined at 84 °C. It is therefore evident that the hemiacetal ester skeletons in MBDO unit were sufficiently stable such that selective thermal cleavage of the hemiacetal ester did not occur.

Acid hydrolysis of the (co)polymers was expected to produce a polyketone having a 1,3-dicarbonyl structure in the repeating units. To assess this possibility, aqueous 1 M HCl

equimolar to the MBDO units was added to a solution of poly(MBDO) in DMSO- $d_6$  and the reaction mixture was heated at 80 °C. The reaction was monitored using  $^1\text{H}$  NMR spectrometry [Figure 4(a)]. After 12 h, the broad signals due to the poly(MBDO) decreased and a set of new sharp signals, assignable to acetic acid (1.89 ppm) and salicylic acid (7.75, 7.48 and 6.91 ppm) appeared. The reaction proceeded very slowly but the poly(MBDO) signals were found to be almost completely absent after five days.<sup>42</sup> The reaction was also tracked by acquiring DOSY NMR spectra (Figure S5), and the data again suggested gradual polymer degradation to generate small molecules; the diffusion coefficients ( $D_s$ ) for the NMR signals at 7.75, 7.48 and 6.91 ppm and at 1.89 ppm also indicated the formation of salicylic acid and acetic acid, respectively. These compounds were also observed in  $^{13}\text{C}$  NMR spectrum of the reaction mixture (Figure S7). If the acid hydrolysis proceeded in a general path for hemiacetal ester, poly(MBDO) should be decomposed to salicylic acid and polyketone (Scheme S1, F). However, the DOSY NMR spectrum after 5 days indicates that signals assignable to the polymer backbone has comparable  $D$  to those for broad aromatic signals [Figure S5(c)]. Therefore, the remaining polymer fraction kept the aromatic pendant and thus was not the polyketone. These results implies that the main chain scission described in Scheme S1 should have proceeded under these conditions to afford salicylic acid and acetic acid, instead of the deprotection of hemiacetal ester to polyketone and salicylic acid.<sup>43</sup> The concurrent decrease in the molecular weight of the sample during acid hydrolysis of the polymer was assessed using the copolymer in Entry 3, Table 1 (which showed good solubility in THF). Similar to the results obtained using poly(MBDO),  $^1\text{H}$  NMR signals for acetic acid and salicylic acid were observed after five days [Figure 4(b)], while the  $M_n$  value gradually decreased from 37,500 to 2000 [Figure 4(c) and Figure S8].<sup>44</sup> If the degradation process began solely at the MBDO units at the chain ends, the decomposition would be expected to terminate when the degradation front reached a VAc unit. Therefore, the significant decrease in  $M_n$  and almost complete disappearance of MBDO units suggest that the degradation instead occurs both at the chain ends and internal MBDO units.



**Figure 4.** Variations in the  $^1\text{H}$  NMR spectra during the acid hydrolysis of (a) the MBDO homopolymer and (b) the copolymer in Entry 3, Table 1 (400 MHz, DMSO- $d_6$ , 25 °C). S: Salicylic acid, A: Acetic acid, ●: H<sub>2</sub>O and \*: DMSO. (c)  $M_n$  as a function of time during the acid hydrolysis of the copolymer.

## Conclusions

MBDO, a cyclic ketene hemiacetal ester prepared from acetyl salicylic acid, exhibited higher reactivity than VAc during radical polymerization to afford a cyclic hemiacetal ester structure. The MBDO units in the resulting polymer could be degraded to acetic acid and salicylic acid by acid hydrolysis. Since these decomposition products are the starting materials for MBDO, vinyl polymers based on MBDO are potentially recyclable. The incorporation of MBDO units into common vinyl polymers would also be expected to produce degradable materials. Although this is a fundamental research, the results have presented a great hint to develop a recyclable vinyl polymer.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

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- The expanded <sup>1</sup>H NMR spectrum after 7 days is available in **Figure S6**, although the experiment lot is different from that for **Figure 4(a)**.
- This is a speculation from the resulting products, and further investigation to understand the degradation mechanism are currently underway in our laboratory.
- The VAc units should be decomposed to vinyl alcohol units, as the <sup>1</sup>H NMR signals for the methine group of VAc units disappeared after five days [**Figure 4(b)**]. However, the direct observation of vinyl alcohol units was impossible, as the signals were broad and overlapped with those for H<sub>2</sub>O and remaining copolymers.
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