

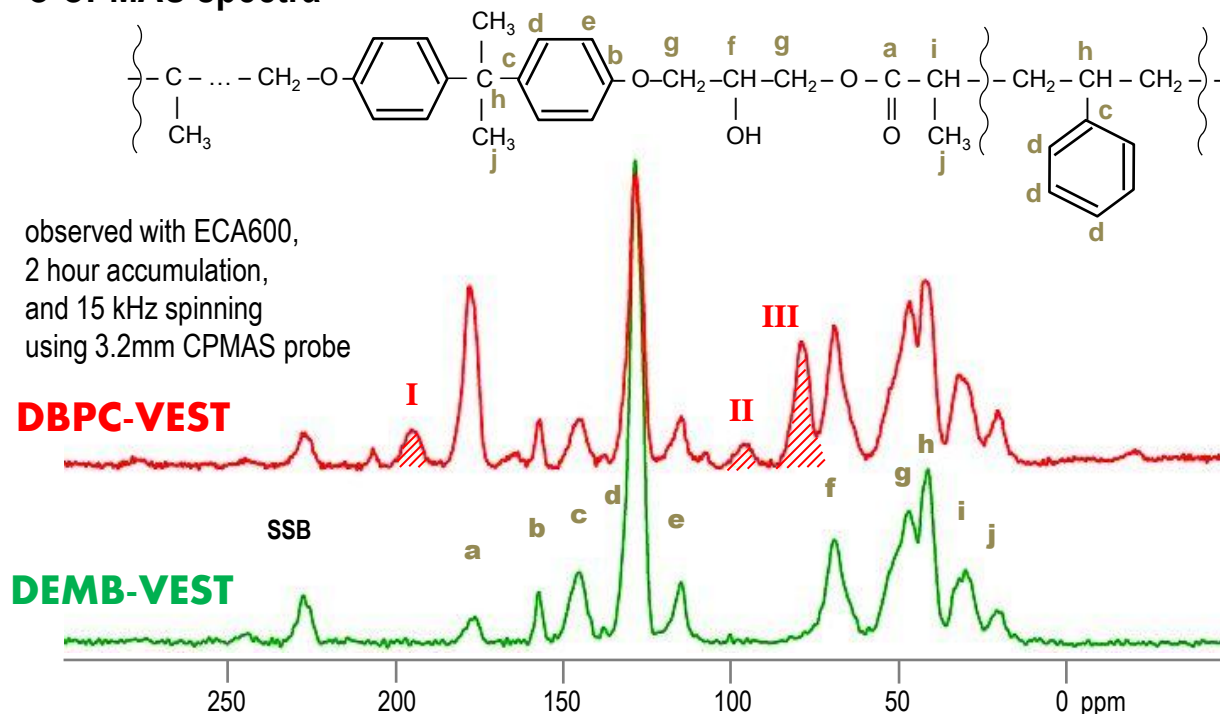
# Microstructures of Vinyl Ester Resins Clarified by Solid-state $^{13}\text{C}$ Chemical Shifts and $^{13}\text{C}$ $T_{1\rho}$ Relaxation Times

Vinyl ester resins are used as adhesives and insulators of electrical equipment, and their novel polymerization methods are investigated for their higher thermostability. It was reported [1] that the living radical polymerization of vinyl ester monomers (VE) and styrene monomers (ST) with the initiator of alkyl borane DEMB (diethylmethoxyborane) improves the thermostability of vinyl ester resins compared with those obtained with the conventional initiators of AIBN (azobisisobutyronitril) and DBPC (1,1-di(*t*-butylperoxy)cyclohexane). In addition to the reported macroscopic physical properties such as thermal weight loss, the information of the microscopic structures of the materials may play an important role for understanding the physical properties and further improvement of the materials. This note introduces a research on the different microstructures of vinyl ester resins produced with various polymerization initiators studied by  $^{13}\text{C}$  NMR [2].

¶ The experimental results were obtained by cooperation with Hitachi Ltd. and Hitachi Power Solutions Co., Ltd.

Figure shown below are the  $^{13}\text{C}$  CPMAS spectra of vinyl ester resin produced with the initiator DBPC (DBPC-VEST) and that with DEMB (DEMB-VEST). Almost all the lines are assigned to the carbons of the plausible structures of these vinyl esters.

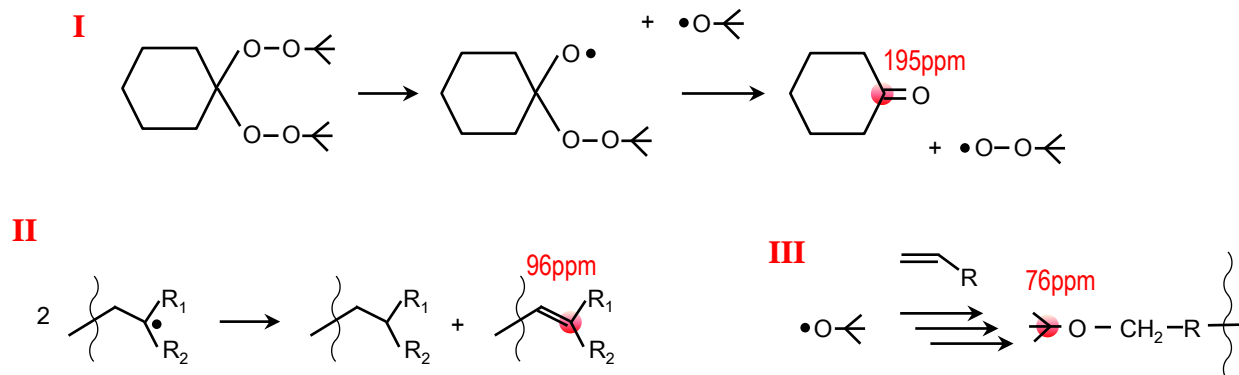
## $^{13}\text{C}$ CPMAS spectra



[1] T. Muraki, S. Amou, H. Morooka, H. Kagawa, K. Souma, *Network Polymer*, **34(4)**, 178 (2013).

[2] Y. Kajihara, T. Muraki, *Network Polymer*, **35(4)**, 161 (2014).

On the other hand, three additional lines (I, II, III) are detected for DBPC-VEST compared with DEMB-VEST. These lines are considered to be assigned to decomposition of DBPC (I), disproportionation of vinyl compound derivative (II), and polymerization addition reaction (III). Especially on disproportionation (II), the spectrum of DEMB-VEST shows that its terminal double bonds are much less than those of DBPC-VEST, consistent with the result of thermal weight loss.



We measured the  $^{13}\text{C}$   $T_{1\rho}$  (longitudinal relaxation time in the rotating frame) and list the results in Table. The values of  $^{13}\text{C}$   $T_{1\rho}$  are found to greatly decrease in the order of DBPC > AIBN > DEMB.

In general,  $^{13}\text{C}$   $T_{1\rho}$  values decrease when exist many of microscopic molecular motions whose speed matches with the applied spin-lock RF strength (30 kHz in this study). Table indicates that such slow motions occur in DEMB-VEST very frequently.

Carbon #	Chemical Shift (ppm)	$T_{1\rho}$ ( $^{13}\text{C}$ ) (ms)		
		DBPC-VEST	AIBN-VEST	DEMB-VEST
<b>a</b>	<b>178.0</b>	<b>11.5</b>	<b>30.4</b>	<b>10.2</b>
<b>b</b>	<b>157.1</b>	<b>58.1</b>	<b>29.1</b>	<b>11.5</b>
<b>c</b>	<b>144.4</b>	<b>31.8</b>	<b>21.9</b>	<b>8.2</b>
<b>d</b>	<b>128.1</b>	<b>8.5</b>	<b>6.4</b>	<b>1.6</b>
<b>e</b>	<b>114.7</b>	—	<b>5.1</b>	<b>2.4</b>
<b>f</b>	<b>68.7</b>	<b>4.7</b>	<b>4.6</b>	<b>0.7</b>
<b>h</b>	<b>46.1</b>	<b>10.1</b>	<b>9.6</b>	<b>2.9</b>
<b>i</b>	<b>31.0</b>	<b>16.1</b>	<b>12.9</b>	<b>5.1</b>
<b>j</b>	<b>19.7</b>	<b>16.5</b>	<b>13.6</b>	<b>6.0</b>

Also,  $T_{1\rho}$  as well as  $T_2$  is known to relate with the density of microscopic cross linkings; the larger cross-linking density materials have, the shorter their  $T_{1\rho}$  (and  $T_2$ ) becomes [3]. The above Table suggests that the cross-linking densities become larger in the order of DBPC < AIBN < DEMB, and this fact is consistent with the physical properties of glass-transition temperatures and elastic modulus of rubber phase [1].

Thus, NMR is prospective to clarify the origin of macroscopic physical properties and may provide the microscopic information useful for materials developments.

[3] K. Fukumori, Toyota Central Labs. R&D Review, **28**, 11 (1993).