ORIGINAL ARTICLE

Viscoelastic properties and birefringence of phenolic resins

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Dynamic viscoelasticity and dynamic birefringence of phenolic resins having different cross-linking density were examined to clarify the relationship between structure and viscoelastic properties. Dynamic modulus was found to be insensitive to cross-linking density at a high cross-linking density, where molar mass between the cross-linking points was smaller than the viscoelastic segment size of phenolic resin, whereas the complex strain-optical coefficient reflects more sensitively the cross-linking density.

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INTRODUCTION

Phenolic resins are the earliest commercial synthetic resin and are used for various applications, for example, circuit boards, mold products, adhesives and so on.^{1–3} Phenolic resins are thermosetting plastics, and they are neither soluble in solution nor melted after subjected cure reactions. For this reason, the characterization methods of phenolic resins are very limited and therefore the relationship between mechanical properties and structure of phenolic resins are not well-understood. Usually, cure reactions are characterized by thermal or spectroscopy measurements. In thermal measurement, it is possible to know the curing ratio by the heat of reaction. The residual ratio of the functional group of resins or cure agents is determined by spectroscopy. However, thermodynamics of phenolic resins are very complicated and chemical reaction of phenolic resins is not clearly understood because of the complex polymerization process. Therefore, results of thermal measurement or spectroscopy have been utilized to estimate cross-link density of phenolic resins qualitatively.

For linear polymers, molecular origin of stress in the rubbery state can be described with coarse-graining molecular models.⁴ In these models, the chain is divided into viscoelastic segments. The rubbery stress can be related with anisotropic chain conformation and therefore can be described with the orientation of segments. This molecular picture is supported by the stress-optical rule.⁵ For the case of polystyrene, the viscoelastic segment is composed of about ten repeating units.⁶ On the other hand, thermosetting plastics form highly cross-linked network structures, and sometimes the strand between two cross-linking points can be smaller than the viscoelastic segment size. For such a case, the viscoelastic properties cannot be described with ordinary coarse-graining molecular models.

Another complication of phenolic resins is the inhomogeneous network structure. Usually, the cross-linking reaction progresses

inhomogeneously and the resulting network structure becomes inhomogeneous. Cross-linking density is not uniform in the system.

In this study, we measured viscoelastic properties and strain-induced birefringence of phenolic resins with various degrees of cross-linking around the glass transition region to clarify the molecular origin of stress for highly cross-linked networks.

EXPERIMENTAL PROCEDURE

We used phenolic moldings of random novolac (NV), purchased by Sumitomo Bakelite Co, Ltd as a phenolic resin and 1,3,5,7-tetraazatricyclo(3.3.1.1 (3,7)) decane (Hx: hexamethylenetetramine) purchased by CCP Co, Ltd as a cure agent (see Figure 1). The weight averaged molar mass, M_w , and the number averaged molar mass, M_n , of the random novolac were measured as $M_w = 4.4 \times 10^3 \text{ g mol}^{-1}$ and $M_n = 9.5 \times 10^2 \text{ g mol}^{-1}$, with a gel permeation chromatography (Tosoh, Tokyo, Japan) and a right-angle light scattering/visco detector (TDA302; Viscotek, Worcestershire, UK). Degrees of cross-linking of phenolic moldings were changed by the amount of cure agent 1.6–6.0 wt%. T_g of samples are measured by modulated DSC (DSC2910, TA Instrument, New Castle, DE, USA). Result of DSC was shown in Figure 2 and Table 1. T_g increased with increasing of amount of the cure agent.

Viscoelastic and birefringence properties of phenolic resins are measured by a tensile type rheometer (Rheospectoler DVE 3, Rheology Co, Ltd.) attached with an optical systems at several temperatures between $T_g - 30 \text{ K}$ and $T_g + 30 \text{ K}$ in frequency 1–130 Hz. Details of the apparatus were published elsewhere.⁶ For novolac, shear measurements were utilized with a home-built apparatus. Details of the shear apparatus have been already reported.^{7,8} The measurement mode of viscoelasticity and birefringence are shown in Table 1.

RESULTS

Figure 3 shows the complex shear modulus, $G^*(\omega) = G'(\omega) + iG''(\omega)$ and the complex strain-optical coefficient, $K^*(\omega) = K'(\omega) + iK''(\omega)$, which is the complex ratio of shear birefringence component, n_{12} , of

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Figure 1 Chemical structures of novolac and cure agent (hexamethylenetetramine).

Figure 2 Differential scanning calorimetry of phenolic resins. A full color version of this figure is available at *Polymer Journal* online.

refractive index tensor to the strain, of random novolac at a reference temperature of 393 K. For amorphous polymers, the relationship between birefringence and stress can be written with the modified stress-optical rule (MSOR).⁶ MSOR says that both the stress and birefringence have two components, rubbery and glassy components. The rule for shear quantities can be expressed as follows.

$$G'(\omega) = G'_R(\omega) + G'_G(\omega) \quad (1)$$

$$K'(\omega) = K'_R(\omega) + K'_G(\omega) = C_R G'_R(\omega) + C_G G'_G(\omega) \quad (2)$$

Here, quantities having subscript, $i=R$ and G , stand for the component functions and C_i is the stress-optical coefficient for the component i . In a previous study on random novolacs, we determined $G'_R(\omega)$ and $G'_G(\omega)$, and we showed that random novolacs have randomly branched structure.⁹ The stress-optical coefficient, C_R was estimated to $2.2 \times 10^{-9} \text{ Pa}^{-1}$. C_R of linear polymers having similar molecular structure, bisphenol A polycarbonate, is $5.0 \times 10^{-9} \text{ Pa}^{-1}$.¹⁰ Smaller C_R value suggests that novolacs have a relatively flexible chain structure. Accordingly, the estimated viscoelastic segment size for novolacs was 300 g mol^{-1} in the previous study.

Overview of E^* and O^* for phenolic resins

Figure 4 shows the complex Young's modulus, $E^*(\omega) = E' + iE''$ and the complex stress-optical coefficient in tensile deformation, $O^*(\omega) = O' + iO''$, of the four phenolic resins at the reference temperature, $T_r \sim T_g + 10 \text{ K}$. Here, the method of reduced variables¹¹ was used to obtain the composite curve. The superposition worked well, although breakdown of the method of reduced variables was reported for various polymers around the glass-to-rubber transition zone.

Around the glass transition zone, Young's modulus and stress-optical coefficient of Hx/Nv-1.6, relax about two decades in magnitude.

Table 1 Composition and T_g of phenolic resins

Sample name	wt% of cure agent	T_g/K	Cure reaction	Test mode
Random novolac	0	306	none	shear
Hx/NV-1.6	1.6	356	175 °C/6h	tensile
Hx/NV-2.2	2.2	367	175 °C/6h	tensile
Hx/NV-3.1	3.1	382	175 °C/6h	tensile
Hx/NV-6.0	6	444	175 °C/6h	tensile

Figure 3 Viscoelastic properties and birefringence of random novolac. Open symbols are complex shear modulus and closed symbols are complex strain-optical coefficient; circle and square symbols are real and imaginary part of G^* and K^* , respectively. Reference temperature is 373 K.

Young's moduli of Hx/NV-2.2, Hx/NV-3.1 and Hx/NV-6.0 relax about one decade in magnitude irrespective of cross-linking density. On the other hand, the complex strain-optical coefficient strongly depends on cross-linking density. For low cross-linking phenolic resins, Hx/NV-1.6 and 2.2, the shape of O^* is almost the same as E^* . With an increase in the cross-linking density, the relaxation magnitude of O^* decreases. As birefringence mostly reflects the orientation of benzene rings having large anisotropy in phenolic resins, the present results indicate that reorientation of phenolic groups around the glass transition zone is restricted with an increase in the cross-linking density. We note for the case of Hx/NV-1.6, Young's modulus shows two step-wise relaxation as indicated by arrows, whereas O^* shows a single relaxation process. The two step-wise relaxation suggests that the system is not homogenous. We will discuss this issue later.

For further analysis, we determined characteristic quantities. We can define the limiting values for E' at high and low frequencies, $E'(\infty)$ and $E'(0)$. $E'(\infty)$ corresponds to the limiting glassy modulus and $E'(0)$ corresponds to the plateau modulus, E_N , of phenolic resins. Similarly, we define the limiting values for O' , $O'(\infty)$ and $O'(0)$. For some cases, for example, $E'(\omega)$ for Hx/Nv-1.6 gradually decreases with decreasing frequency at low frequencies and the $E'(0)$ value is not clear in double logarithmic scales. For such a case, we extrapolated $E'(\omega)$ at $\omega = 0$ in a linear plot. The typical experimental uncertainty of the limiting values is 10%. The obtained values are summarized in Table 2. The stress-optical coefficient in the rubbery zone can be estimated with $C_R = O'(0)/E'(0)$. C_R values for phenolic resins are smaller than C_R of no cross-linking random novolac and C_R

Figure 4 Viscoelastic properties and Birefringence of Phenolic resins, (a) Hx/NV-1.6, (b) Hx/NV-2.2, (c) Hx/NV-3.1, (d) Hx/NV-6.0. Opened symbols are complex Young's modulus and closed symbols are complex strain-optical coefficient; circle and square symbols are real and imaginary part of E^* and Q^* , respectively. Reference temperatures are (a) 368 K, (b) 377 K, (c) 393 K, (d) 453 K, respectively.

Table 2 Characteristic parameters for phenolic resins

	$E'(0)$ /GPa	$E'(\infty)$ /GPa	$O'(0)$	$O'(\infty)$	$C_R / 10^{-10} \text{Pa}^{-1}$	$C_G / 10^{-11} \text{Pa}^{-1}$	$O_R'(\infty)$	M_C /gmol $^{-1}$
Random novolac	N.A	2	N.A.	0.1	2.2	3.7	0.02	N.A
Hx/NV-1.6	0.02	2	0.0022	0.11	2.1	4	0.05	5900
Hx/NV-2.2	0.1	2.7	0.006	0.085	0.53	2.5	0.03	1200
Hx/NV-3.1	0.11	3	0.015	0.15	1.3	3.6	0.07	900
Hx/NV-6.0	0.055	2.2	0.03	0.12	5.5	3.2	0.05	520

values decreases with increasing cross-linking density, although C_R for amorphous polymers is determined by anisotropy of polarizability of segments. The present result strongly suggests that $E'(0)$ is not determined by the simple rubber network theory.

Estimation of molar mass of network strands from birefringence

Molar mass of network strand between cross-linking points, M_C , has been estimated by the follow equation on the assumption of rubber elasticity.¹²

$$M_C = \frac{\rho RT}{G_N} = \frac{3\rho RT}{E_N} = \frac{3\rho RT}{E'(0)} \quad (3)$$

Here, we assume $E_N = 3G_N$. However, if we applied equation (3) to the present data, we obtain unrealistic results. At Hx/NV-1.6, estimated molar mass of network strands is about 1000 gmol $^{-1}$. On the other hand, at Hx/NV-2.2 to 6.0, estimated molecular weight of network strands is about 100 gmol $^{-1}$. This value is close to phenol and methylene monomer's molecular weight of 108 gmol $^{-1}$, clearly indicating that the traditional theory for rubber elasticity cannot be applied. As we have described earlier, the viscoelastic segments for uncross-linked resin was 300 gmol $^{-1}$. Thus, we cannot estimate the correct M_C value from the rubbery plateau modulus. As we have already seen, C_R varies with cross-linking density. Unrealistic small

M_C values consistently indicate the breakdown of rubber elasticity. We will show that the network structure could be characterized by the birefringence data.

The relationship between birefringence and stress

For ordinary amorphous polymers, the relationship between strain-induced birefringence and stress can be written with the modified stress-optical rule, MSOR.¹³ The MSOR for tensile deformation can be written as follows.⁶

$$E'(\omega) = E'_R(\omega) + E'_G(\omega) \quad (4)$$

$$O'(\omega) = O'_R(\omega) + O'_G(\omega) = C_R E'_R(\omega) + C_G E'_G(\omega) \quad (5)$$

The MOSR is based on the SOR in the rubbery zone. In the rubber zone, the glassy component relaxes completely and therefore $E'_G(\omega) \rightarrow 0$ and $E''_G(\omega) \rightarrow 0$. Thus, equations (4 and 5) reduces the ordinary SOR, $O^*(\omega) = C_R E^*(\omega)$. However, as we have discussed earlier, the SOR does not hold valid for the case of phenolic resins. One possible explanation for the breakdown SOR is the existence of a third component in the rubbery region. As we have already pointed out, Figure 4 shows Young's modulus of Hx/NV-1.6 shows two-step relaxations. This feature strongly suggests that the relationship between birefringence and stress cannot be described with two

components version of MSOR. We speculate that additional relaxation process would be necessary to describe the stress–birefringence relationship. This is probably due to their inhomogeneous structure. In the following section, we analyze O^* in detail. This is because the birefringence mainly reflects the reorientation of segments and therefore the analysis would be easier than the stress relaxation.

Estimation of cross-linking density from birefringence data

The orientational birefringence can be related with the intrinsic birefringence, Δn_0 , and orientation degree of repeating units, f .

$$\Delta n = \Delta n_0 f \quad (6)$$

By using equation 6, we can estimate f from the birefringence. MSOR says that birefringence includes not only the orientational birefringence (R component) but also the glassy component, O_G^* in the glass zone. The contribution of O_G^* may be estimated as follows. In the following, we ignore details of frequency dependence of O_G^* and we just discuss about the limiting behavior at high and low frequencies. At high frequencies, MSOR can be written as follows.

$$O'(\infty) = O'_R(\infty) + O'_G(\infty) = O'_R(\infty) + C_G E'_G(\infty) \quad (7)$$

To the best of our knowledge, the C_G value for polymers containing benzene rings is almost constant $3 \times 10^{-11} \text{ Pa}^{-1}$, irrespective of molecular structure of repeating units, and $E'_G(\infty) \sim E'(\infty)$ is approximately $2 \times 10^9 \text{ Pa}$ for the present phenolic resins. Thus, we can estimate $O'_G(\infty)$ value from $C_G E'_G(\infty)$. Now, $O'_R(\infty)$ value can be estimated as $O'(\infty) - O'_G(\infty)$. Thus, determined values are summarized in Table 2. The $O'_R(\infty)$ value is related with molar mass of viscoelastic segment, M_S of phenolic resins.^{6,13}

$$M_S = \frac{\rho RT}{G'_R(\infty)} = \frac{3\rho RT}{E'_R(\infty)} = \frac{3C_R \rho RT}{O'_R(\infty)} \quad (8)$$

At low frequencies, the glassy component would have relaxed in short times, and therefore we obtain

$$O'(0) = O'_R(0) \quad (9)$$

The $O'_R(0)$ value is related with the molar mass of the network strand.

$$M_C = \frac{\rho RT}{G'_R(0)} = \frac{3\rho RT}{E'_R(0)} = \frac{3C_R \rho RT}{O'_R(0)} \quad (10)$$

For the case of phenolic resins, $E'(0) \gg E'_R(0)$ and therefore, equation (3) provides an unrealistic M_C value. On the other hand, we anticipate that $O'(0) = O'_R(0)$ holds well. Comparing equations (8 and 10), molar mass of the network strand between the cross-links, M_C , may be estimated by the following equation.

$$M_C = M_S \frac{O'_R(\infty)}{O'_R(0)} \quad (11)$$

In the above discussion, we used the SOR. However, the validity of the SOR is not essential. As the birefringence can be related with orientational degree of structure units, as described by equation 6, the ratio, $O'_R(0)/O'_R(\infty)$, can be regarded as the relaxation ratio of orientation, $f(0)/f(\infty)$. According to the molecular theory, the relaxation of segment orientation corresponds to the increase in size of the subchain.¹⁴ The estimated value of M_C from the birefringence relaxation is summarized in Table 2. M_C decreases with increasing cross-linking density, as we expected.

The concentration of the network strand can be estimated from M_C .

$$c_{\text{strand}} = \frac{\rho}{M_C} \quad (12)$$

Figure 5 Comparison of the concentration of network strand estimated from birefringence measurement and concentration of cross-linking agent (open circle). The closed squares represent after correction of contribution of the third hard core component. A full color version of this figure is available at *Polymer Journal* online.

The concentration of the network strand should be related with the concentration of the cross-linking agent.

$$c_{\text{HX}} = \frac{f_C \rho}{M_{\text{HX}}} \quad (13)$$

Here, f_C is the functionality of the cross-linking agent. In the derivation of equation 11, we assumed that the extent of cross-linking reaction is one. We did not check the actual extent of the reaction, but we note that our reaction condition is widely used for molding of phenolic resins and known that the extent of the reaction is close to one. The two concentrations, c_{strand} and c_{HX} are compared in Figure 5.

Figure 5 clearly indicates that the two concentrations, c_{strand} and c_{HX} agree well with each other, except for Hx/NV-1.6 that has the lowest cross-link agent. Thus, M_C obtained from birefringence relaxation is well correlated with the concentration of the cross-linking agent. The data point for Hx/NV-1.6 deviates from the proportionality. This may be related to some other effects, such as entanglements. Thus, we conclude that birefringence measurements are very effective to characterize the network structure.

DISCUSSION

Now, our question is why the rubbery plateau modulus, $E'(0)$, is insensitive to the cross-linking structure. The present analysis indicates that the ordinary stress-optical rule and the modified stress-optical rule composed of two components does not hold well even for Hx/NV-1.6. The rubbery plateau modulus at high temperatures cannot be simply related with the orientation of the network strand. The C_R value depending on cross-linking density also supports this conclusion.

As the two components version of MSOR did not work for phenolic resins, we consider the third component of stress. If the pre polymer, novolac, has a small-hard core, due to its hyperbranched structure, the resulting network would contain the same hard core parts in it. In a previous study, we attribute molecular origin of the glassy component to the reorientational motion of the structure unit around the main-chain axis.^{15,16} According to this interpretation, the branched structure cannot rotate around the main-chain axis.

Thus, branching causes non-relaxation of the glassy component. If we consider such hard cores due to branching as the third component, the MSOR may be written as follows

$$E'(\omega) = (1 - \phi_{\text{HC}})(E'_{\text{R}}(\omega) + E'_{\text{G}}(\omega)) + \phi_{\text{HC}}E'_{\text{HC}} \quad (14)$$

$$O'(\omega) = (1 - \phi_{\text{HC}})(C_{\text{R}}E'_{\text{R}}(\omega) + C_{\text{G}}E'_{\text{G}}(\omega)) + \phi_{\text{HC}}C_{\text{HC}}E'_{\text{HC}} \quad (15)$$

Here, ϕ_{HC} is the volume fraction of hard core parts and E'_{HC} is the constant modulus of the hard cores. In the following, we assume that the hard core part is glassy and does not relax with time even at temperatures higher than the glass transition temperature because of restriction of molecular motion brought by the very high cross-linking density. To discuss the validity of equation (14 and 15), we calculate the limiting values at high and low frequencies. If we further assume $E'_{\text{HC}} = E'_{\text{G}}(\infty)$ and $C_{\text{HC}} = C_{\text{G}}$, we obtain

$$E'(\infty) = (1 - \phi_{\text{HC}})E'_{\text{R}}(\infty) + E'_{\text{G}}(\infty) \quad (16)$$

$$O'(\infty) = (1 - \phi_{\text{HC}})(C_{\text{R}}E'_{\text{R}}(\infty)) + C_{\text{G}}E'_{\text{G}}(\infty) \quad (17)$$

Similarly, at low frequencies, we obtain

$$E'(0) = (1 - \phi_{\text{HC}})(E'_{\text{R}}(0)) + \phi_{\text{HC}}E'_{\text{G}}(\infty) \quad (18)$$

$$O'(0) = (1 - \phi_{\text{HC}})C_{\text{R}}E'_{\text{R}}(0) + \phi_{\text{HC}}C_{\text{G}}E'_{\text{G}}(\infty) \quad (19)$$

Equations (18 and 19) explain why the phenolic resins show the higher plateau modulus and why the ordinary stress-optical rule does not hold. For the modulus in the rubbery zone, significant contribution of the HC component exists in addition to the R components. As $E'(0) \sim 0.1 \text{ GPa} \sim \phi_{\text{HC}}E'_{\text{G}}(\infty) > E'_{\text{R}}(0)$ and $E'_{\text{G}}(\infty) \sim 3 \text{ GPa}$, we estimate that $\phi_{\text{HC}} = 0.03$.

In the previous section, we compare $O'(\infty) - C_{\text{G}}E'_{\text{G}}(\infty)$ and $O'(0)$ to evaluate the M_{C} . According to equations (17 and 18), we should compare $O'(\infty) - C_{\text{G}}E'_{\text{G}}(\infty)$ and $O'(0) - \phi_{\text{HC}}C_{\text{G}}E'_{\text{G}}(\infty)$. Thus, the determined M_{C} is shown in Figure 5. The effect of subtraction of $\phi_{\text{HC}}C_{\text{G}}E'_{\text{G}}(\infty)$ is not so significant if cross-linking density is high.

In summary, we have firstly shown that the birefringence–stress relationship for phenolic resins cannot be described with the ordinary modified stress-optical rule, which works well for most ordinary amorphous polymers. The present analysis shows that phenolic resins are not homogeneous and contain small amount (3 vol%) of non-relaxing hard core, which is probably produced in the pre polymer due to branching. The molecular motion of the structural units at the branching points would be highly restricted and therefore, the units behave as non-relaxing elastic units. Such an inhomogeneous structure or a two-phase structure has been

proposed.¹⁷ Izumi *et al.* showed that linear strands of phenolic resins grow at the beginning of gelation, followed by small structures that form between strands by reaction of cross-linking with small-angle X-ray scattering experiments.¹⁸ Such a scenario for the cross-linking process does not contradict our present conclusion.

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- 1 Baekeland, L. H. Method of making insoluble products of phenol and formaldehyde., USA, Patent 942699 (1907).
- 2 Crespy, D., Bozonnet, M. & Meier, M. 100 Years of Bakelite, the Material of a 1000 Uses. *Angew. Chem. Int. Ed.* **47**, 3322 (2008).
- 3 Gardziella, A., Pilato, L. A. & Knop, A. *Phenolic resins: chemistry, applications, standardization, safety and ecology* (Springer, Berlin, 1999).
- 4 Doi, M. & Edwards, S. F. *The Theory of Polymer Dynamics* 391 (Clarendon, Oxford, 1986).
- 5 Janeschitz-Kriegl, H. *Polymer Melt Rheology and Flow Birefringence* 524 (Springer-Verlag, Berlin, 1983).
- 6 Inoue, T., Okamoto, H. & Osaki, K. Birefringence of Amorphous Polymers I Dynamic Measurement on Polystyrene. *Macromolecules* **24**, 5670–5675 (1991).
- 7 Iwawaki, H., Inoue, T. & Nakamura, Y. Rheo-Optical Study on Dynamics of Bottlebrush-Like Polymacromonomer Consisting of Polystyrene. *Macromolecules* **44**, 5414–5419 (2011).
- 8 Iwawaki, H., Urakawa, O., Inoue, T. & Nakamura, Y. Rheo-Optical Study on Dynamics of Bottlebrush-Like Polymacromonomer Consisting of Polystyrene. II. Side Chain Length Dependence on Dynamical Stiffness of Main Chain. *Macromolecules* **45**, 4801–4808 (2012).
- 9 Maji, S., Urakawa, O. & Inoue, T. Rheo-optical study of structure and viscoelasticity of novolacs (2013).
- 10 Hwang, E. J., Inoue, T. & Osaki, K. Viscoelasticity and birefringence of bisphenol-A polycarbonate. *Polymer. (Guildf)* **34**, 1661–1666 (1993).
- 11 Ferry, J. D. Dependence of Viscoelastic Behavior on Temperature and Pressure. In *Properties of Polymers*, 4th edn, Ch. 11, 264 (Wiley, New York, USA, 1980).
- 12 Treloar, L. R. G. *The Physics of Rubber Elasticity* (Clarendon press, Oxford, Great Britain, 1958).
- 13 Inoue, T. & Osaki, K. Role of polymer chain flexibility on the viscoelasticity of amorphous polymers around the glass transition zone. *Macromolecules* **29**, 1595–1599 (1996).
- 14 Kuhn, W. & Gr $\ddot{u}$ n, F. Beziehungen zwischen elastischen Konstanten und Dehnungsdoppelbrechung hochelastischer Stoffe. *Kolloid Z.* **101**, 248–271 (1942).
- 15 Inoue, T., Matsui, H., Murakami, S., Kojiya, S. & Osaki, K. Strain-induced birefringence and molecular structure of glassy polymers. *Polymer. (Guildf)* **38**, 1215–1220 (1997).
- 16 Inoue, T., Matsui, H. & Osaki, K. Molecular origin of viscoelasticity and chain orientation of glassy polymers. *Rheol. Acta* **36**, 239–244 (1997).
- 17 Misra, S. C., Manson, J. A. & Sperling, L. H. Epoxy resins Chemistry. *ACS Symposium* **114**, 157 (1979).
- 18 Izumi, A., Nakao, T. & Shibayama, M. Gelation and cross-link inhomogeneity of phenolic resins studied by ^{13}C -NMR spectroscopy and small-angle X-ray scattering. *Softmater* **9**, 4188–4197 (2013).