

# Evidence for spatial heterogeneities observed by frequency dependent dielectric and mechanical measurements in vinyl/dimethacrylate systems

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## Abstract

Frequency dependent dielectric measurements (FDEMS), dynamic mechanical rheometer measurements (DMA) and modulated differential scanning calorimetry (DSC) are applied to observe the formation of a spatial heterogeneity in dimethacrylate/divinylbenzene (D121/DVB) and dimethylacrylate/styrene (D121/St) network systems. The structure evolution information during the reaction, such as  $T_g$ , the dielectric relaxation and the dynamic mechanical relaxation obtained from these measurements for both systems are compared. The result shows that a spatial heterogeneity does exist in both systems. This is based on the existence of two distinct separate relaxation peaks in the dielectric spectrum, two  $T_g$ 's in the DSC profile and the dynamic mechanical analysis. These two regions are ascribed to the formation of microgel regions as previously identified by dynamic light scattering and monomer/oligomer regions. The experimental spectra are affected by the comonomer structure. The breadth of the relaxation distribution of the spatial heterogeneity of the microgel region in the DVB comonomer system is extremely large compared to the large breadth in the styrene system.

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## 1. Introduction

Frequency dependent dielectric measurements (FDEMS) monitor the dipolar reorientation motion of molecules at different time scales in a polymer. Thus, dielectric measurements are an insightful method to monitor chemical and physical property changes. It can be effective for monitoring a variety of properties such as reaction onset, viscosity, degree of cure, buildup in glass transition, material aging, film formation and recrystallization [1–12]. In a previous paper [12], we reported on a new application of FDEMS to detect the structural evolution and spatial heterogeneity formation during dimethacrylate/styrene (D121/St) isothermal cure. Two distinct regions that related to the dipolar mobility in monomer/oligomer and microgel/microgel clusters were characterized by FDEMS. This property of a D121/St network was also verified with differential scanning calorimetry (DSC).

In this paper, we investigate the existence of a dynamic and spatial heterogeneity during the network formation of a D121/DVB system, another dimethacrylate-based system with high cross-linking density. Various techniques are applied to characterize the heterogeneity formation during the cure. The results are compared with the D121/St system. The objective for this work is to understand how the chemical structures and cross-linking density affect microgel formation and its spatial distribution. This paper focuses on the evolution of the dipolar dielectric loss as the sample cures at different temperatures and achieves different degrees of conversion. The differences between the D121/St and D121/DVB systems are presented and discussed. DSC and dynamic mechanical measurements for these two systems provide additional information on the influence of comonomer structure on the network formation and its spatial heterogeneity.

## 2. Experimental section

### 2.1. Materials

Two reactive systems were used in this study, dimethacrylate/divinylbenzene (D121/DVB) and dimethacrylate/styrene

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Table 1  
Chemical products used in synthesis of materials

Name	Chemical formula
Dimethacrylate of tetraethoxylated bisphenol (D121)	
Styrene (St)	
Divinylbenzene	
1-Dodecanethiol	$\text{CH}_3(\text{CH}_2)_{11}\text{SH}$
Azobis(methyl-butyrionitrile)	

(D121/St). Two comonomers (20 wt%) divinylbenzene (DVB) from Fluka and styrene from Aldrich were used. Each was mixed with dimethacrylate of tetraethoxylated bisphenol A (D121) from Akzo-Nobel (80 wt%) separately. 0.5 wt% of chain transfer agent 1-dodecanethiol (Aldrich) and 0.2 wt% of thermal initiator azobis(methylbutyrionitrile) (Aldrich) were added to the reactive ingredients. All products were used as received. Table 1 shows the formulas of these reactants.

Mixing was carried out in a glass vial with a magnetic stirrer and Argon bubbling at ambient temperature for 30 min to ensure a homogeneous blend of all components and to remove oxygen in order to avoid inhibition. Further details of the sample preparation have been previously described in papers by L. Rey et al. [13,14].

## 2.2. Dielectric impedance measurements

The liquid mixture was introduced into a mold made of two glass plates separated by a 4 mm-rubber gasket. A thin sample was needed to maintain a constant temperature during this exothermic reaction. A microsensor from Century Circuit and Electronics, consisted of inter-digitated copper electrodes (50  $\mu\text{m}$  in width with a spacing of 86  $\mu\text{m}$ ) on an area of  $2.5 \times 1.2$  cm flexible polyimide substrate which was enclosed in the cell. The electrodes were linked to a HP 4192A impedance analyzer by wires to measure the conductance and capacitance of the materials over a range of temperature and frequency.

The enclosed cell was placed in an oven at a constant temperature for cure. The dielectric permittivity and dielectric loss were measured at several frequencies in the range from 50 Hz to 500 kHz. The measurement was taken every 2 s across all 10 frequencies. A computer acquired the dielectric data automatically. The frequency dependence of the dielectric data was used to monitor changes in the dielectric properties versus time during cure and then versus temperature for samples at various degrees of conversion. The frequency dependence of the dielectric loss was used to characterize changes in the  $\alpha$ -relaxation processes of the glass transition during the polymerization and to investigate the existence of two distinct dynamic regions in the system at certain extents of the cure.

## 2.3. DSC measurement

### 2.3.1. Kinetics

A TA 2920 modulated DSC was used for the thermokinetic studies. The thermal analysis consisted of an isothermal DSC run to determine total reaction heat  $Q_i$  at that temperature and then followed by a dynamic ramp to a suitable high temperature to determine the residual heat of polymerization  $Q_r$  for all the samples. The conversion at a given time,  $\alpha(t)$ , was calculated from:

$$\alpha(t) = \frac{Q_t}{Q_r + Q_i} \quad (1)$$

where  $Q_t$  is the heat produced by the reaction at the time  $t$ . These heats are a combination of the heats given off by all double bond reactions in the system, and thus, represents an approximation of the extent of double bond conversion. However, since in this 80% dimethacrylate and 20% vinyl mixture by weight, the dimethacrylate and vinyl double bonds react at the same rate, this approximation is quite accurate. In addition, the system does contain a chain transfer agent, which favors copolymerization. These two observations support the view that the polymerization forms a random copolymer. Further details of the reaction were reported previously [13,14].

### 2.3.2. Glass transition ( $T_g$ ) measurement

During the 70  $^{\circ}\text{C}$  isothermal cure, the reactant in DSC pan was quenched to  $-100$   $^{\circ}\text{C}$  after reacting for a period of time, then heated up to 70  $^{\circ}\text{C}$  at 5  $^{\circ}\text{C min}^{-1}$  to characterize the glass transition at different conversions using inflexion point criteria as determined by the TA instruments software.

## 2.4. Rheology

A TA instrument AR 1000 rheometer was used to measure the viscosity changes and detect the gelation during the isothermal cure: 40 mm diameter aluminum parallel plates separated with a sample thickness of 2 mm were used in the measurements. Liquid monomer were loaded and housed inside an environmental test chamber. The storage modulus  $G'$ , loss modulus  $G''$  and  $\tan \delta$  were measured at regular intervals,

from 0.1 Hz to 1 kHz, at zero normal force. The gel point was determined from the time at which  $\tan \delta$  became independent of frequency [15–19]. This is the point in time when the values of  $\tan \delta$  measured at different frequencies become equal and crossover each other. The gel times are in agreement with previously reported values [14].

Dynamic mechanical measurements were performed in torsion mode with a frequency of  $6.28 \text{ rad s}^{-1}$ . Samples were rectangular bars, 1.5 mm thick, and overall dimension  $20 \times 10 \text{ mm}^2$ ,  $G'$ ,  $G''$  and  $\tan \delta$  have been recorded as a function of temperature.

### 3. Results and discussion

#### 3.1. Isothermal polymerization

Fig. 1(a) and (b) shows the loss component  $\epsilon''$  of the permittivity scaled by the frequency versus time during the  $70^\circ\text{C}$  isothermal cures for both two systems. As discussed previously [4,5], a plot of  $\omega^*\epsilon''$  is a particularly informative

representation of the ion and dipole mobility changes during cure. The overlapping of  $\omega^*\epsilon''$  indicates that the translational diffusion of charge is the dominant physical process at low frequency. Similarly, the peaks of  $\omega^*\epsilon''$  at high frequency indicate the contribution of the dipolar  $\alpha$ -rotational diffusion processes with the buildup in  $T_g$  (Table 2).

The gel time and the change in the dipolar loss due to changes in charge translational diffusion of ions are shown in Fig. 1. For both systems, the gel point is not related to an inflexion point in the changing conductivity. Furthermore, the gel point does not appear to relate to any dielectric event in the dielectric spectra. This phenomenon is undoubtedly because as the gel develops the viscoelastic properties of the resin involves the cooperative motion of many chains while the translational diffusion of the ions continues to involve motions over much smaller molecular dimensions and within the monomer/oligomer region.

Compared to the D121/St system, the D121/DVB has much broader dynamic relaxation peaks (Fig. 1). It also has a much slower polymerization rate (Fig. 2), although the unit number

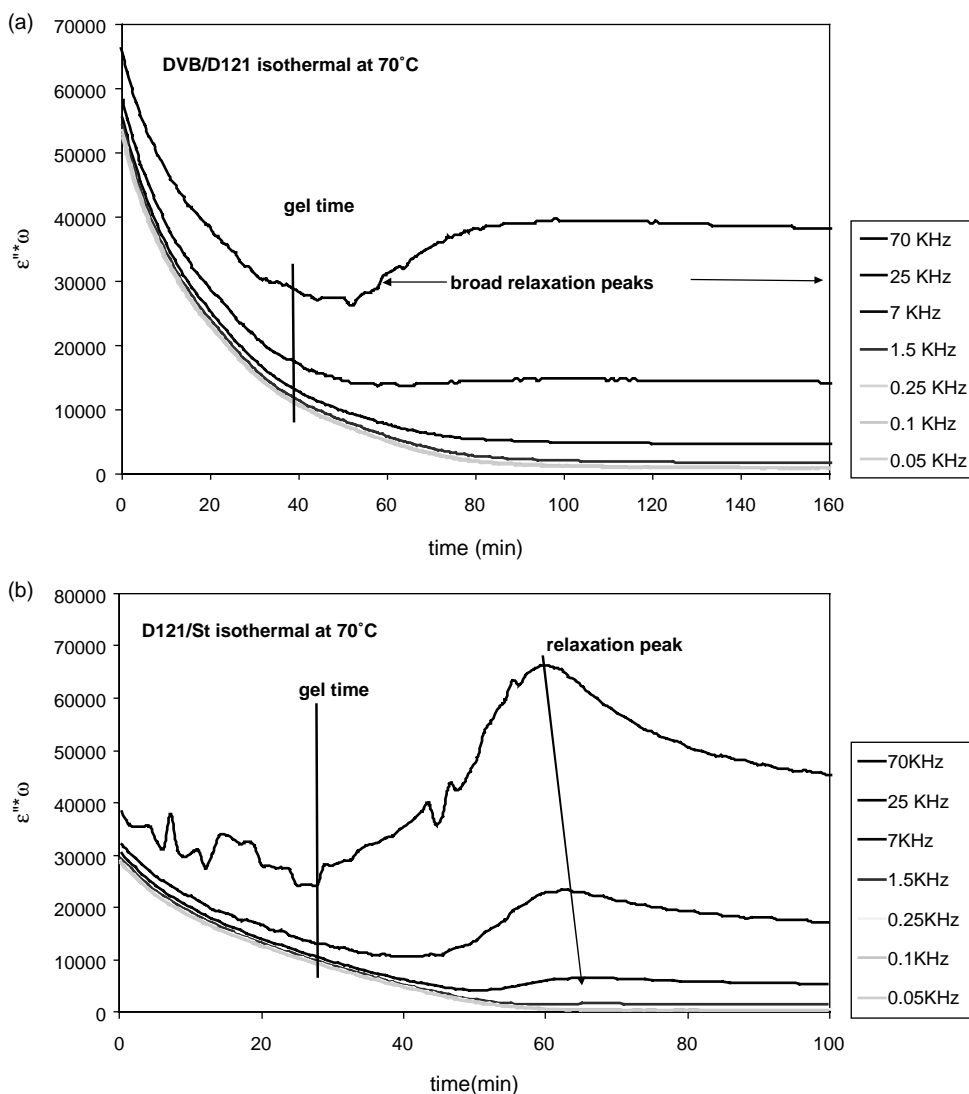


Fig. 1. (a) and (b)  $\epsilon''*\omega$  versus time during  $70^\circ\text{C}$  isothermal polymerization of D121/DVB and D121/St. The lowest three frequencies lie on top of each other.

Table 2  
Total conversions at different curing cycles for D121/St and D121/DVB

D121/St		D121/DVB	
Time (min)	Total conversion* (%)	Time (min)	Total conversion* (%)
0	0	0	0
15	5	35	5
30	19	60	21
50	41	100	42
70	88	150	77

\* Acrylic and styrene monomers.

of double bonds is higher. The presence of DVB has a complex influence on the polymerization. On one hand, the additional cross-linking facilitates the gel formation leading to an auto acceleration effect. On the other hand, the propagation rate is influenced by the diffusion rate of the reactive species. Because the D121/DVB system generates a higher cross-linked structure, the diffusion rate and thereby the polymerization rate is reduced and lower than in the D121/St system.

The broadness of peaks in the dielectric loss  $\omega^* \epsilon''$  plot relates to the length scales of the cooperative relaxation region. It can be used to characterize the width of the distribution of the relaxation times. The broader relaxation peak in D121/DVB system indicates a much larger range of cooperativity length scales during cure compared to D121/St.

### 3.2. Network heterogeneity and morphology

The dielectric, thermal and mechanical properties of each resin at different conversions are important to understanding the chemical structural and the molecular dynamics during network formation and growth. Thus, another temperature–time reaction procedure shown in Fig. 3 was used to investigate the properties of each system at differing extents of reaction. These experiments were carried out in a TA instruments environment chamber with a temperature range of  $-100$  to  $300$  °C.

In this procedure, the monomer mixture was cooled to  $-100$  °C and heated back to  $70$  °C at a constant rate. Then, it

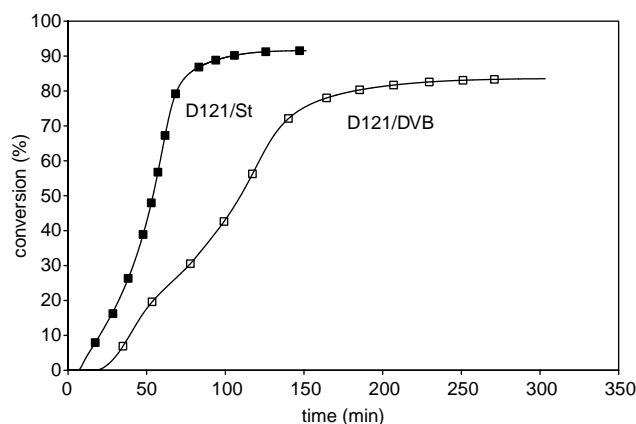


Fig. 2. Monomers conversion during  $70$  °C isothermal cure for D121/DVB and D121/St.

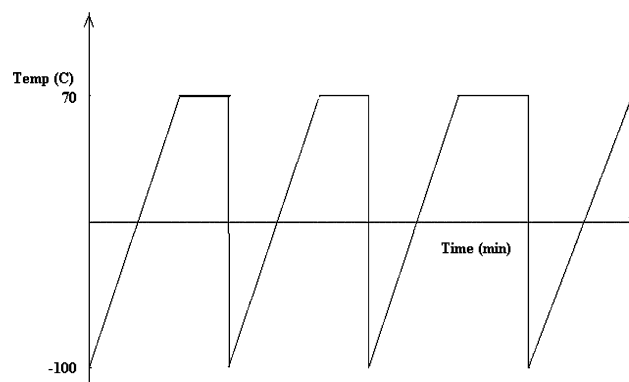


Fig. 3. Temperature ramp procedure.

was held at the curing temperature for a period of time. After the reactant was partially reacted, it was quenched again to  $-100$  °C and heated back to the  $70$  °C at a constant rate. The quenching and heating steps are repeated several times till the system is cured. Table 3 shows the extent of conversion for each cycle measured by DSC.

#### 3.2.1. Dielectric spectroscopy

First, we examine the information in the cure sequence shown in Fig. 3 using dielectric sensing. Fig. 4(a)–(c) display the evolution of  $\alpha$ -relaxations with the advancement of the reaction. In the D121/DVB (Fig. 4(a)) and in the D121/St system (Fig. 4(c)), only the  $\alpha$ -relaxation peak associated with the  $T_g$  for the monomer is observed before the reaction. Previously during the course of this reaction, microgels of increasing size and concentration have been isolated and characterized by dynamic light scattering [14]. In addition, dielectric spectrum of a similar cured acrylic system with two relaxation regions has been suggested to be due to a spatial heterogeneity arising from regions of monomer pools and separate regions of microgels [20,21]. Here, the evolution of the dielectric, DSC glass transition and the dynamic mechanical relaxation spectra are examined in the context of the known formation of microgels and to verify the hypothesis of a true spatial heterogeneity arising from regions of monomer–oligomers and regions of microgel clusters.

Table 3  
 $\alpha$ -Transition temperature measured by FDEMS, DMA and DSC for D121/St and D121/DVB around 20% conversion

	FDEMS (2.5 kHz) (°C)	DMA (2 Hz) (°C)	DSC (°C)
D121/St <sup>a</sup>			
Monomer/oligomer	−45	−25	−60
Microgel/polymer	0	−7	−13
D121/DVB <sup>b</sup>			
Monomer/oligomer	−30	−25	−58
Microgel/polymer	24	8	−35

<sup>a</sup> D121/St sample for FDEMS and DSC measurements is at 19% conversion and for DMA measurement is at 22% conversion.

<sup>b</sup> D121/DVB sample for FDEMS and DSC measurements is at 21% conversion and for DMA measurement is at 24% conversion.

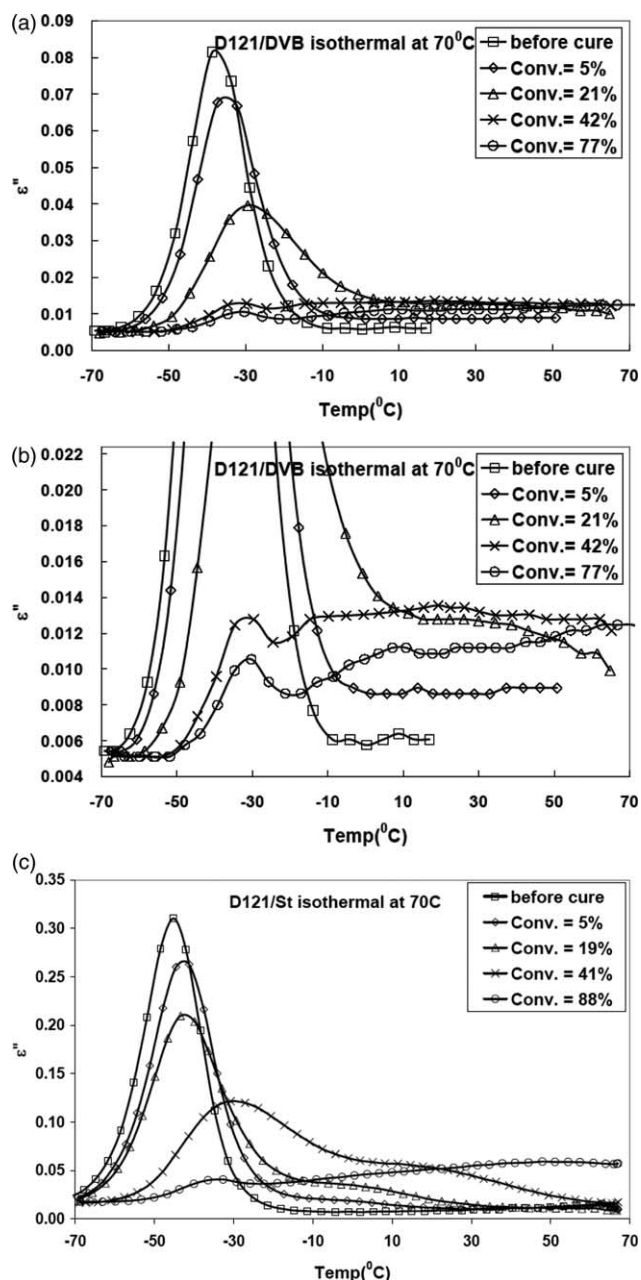


Fig. 4. (a)–(c)  $\epsilon''$  (measured at 2.5 kHz) versus temperature at different degrees of conversion for D121/DVB and D121/St.

During the early stages of the reaction, the dielectric spectra show that as the conversion increases, the magnitude of the original monomer  $\alpha$ -relaxation peak decreases, and the shape of that peak becomes broader. These changes can be explained by the decrease of monomer concentration and formation of oligomers.

During the cure of the D121/DVB and the D121/St, another distinct relaxation peak to be associated with microgel/microgel clusters is formed in the dielectric spectra. For D121/St, this occurs at the early stage of the reaction ( $\alpha=0.05$ ). This peak advances to a higher temperature and becomes broader with the increase of conversion (Fig. 4(c)). The strength and shape changes of the microgel/microgel cluster relaxation peaks

reflect the evolution of network formation and the existence of the spatial heterogeneity in the D121/St system.

Compared with the D121/St system, the changes in the D121/DVB monomer/oligomer  $\alpha$ -relaxation peak show the same tendency but with a larger broadening effect as the reaction advances (Fig. 4(a) and (b)). For example, at  $\alpha=0.21$ , the D121/DVB monomer/oligomer relaxation peak spreads from  $-50$  to  $10$  °C. However, at the same conversion, the relaxation peak for D121/St monomer/oligomer only extends from  $-50$  to  $-10$  °C. In contrast to the D121/St system, a less distinct relaxation peak associated with microgel/microgel clusters is observed at different degrees of cure for D121/DVB. Rather in D121/DVB, the microgel/microgel clusters particles appear to create a flat, very broad relaxation peak, which is less easily discerned in the dielectric spectra (Fig. 4(a) and (b)). The relaxation of the microgels with small particle size overlaps into the monomer/oligomer relaxation and it extends to a high temperature. This peak in the relaxation spectrum is highly skewed toward a broad, flat spectrum with increasing high temperature, which encompasses the relaxation properties of the microgel and microgel clusters.

The diameter distribution of the microgels in the D121/St and D121/DVB systems has been investigated with dynamic light scattering (DLS) during the early stages of the reaction [14]. The D121/DVB system has a much broader distribution in particle size (3–355 nm) with a high percentage (49%) of relatively small particles (3–14 nm). In contrast, the D121/St system forms more uniform, large particles (75–158 nm) at low conversion along with small particles (3–40 nm). As a result, the D121/St system has two distinct relaxation peaks in the dielectric spectra. The broad distribution in size of the microgels in D121/DVB and overall the very broad overlapping relaxation of these two regions supports the much broader distribution in size and suggests a higher heterogeneous nature of D121/DVB. The differing sizes of the microgels in each system provide direct evidence for the difference in their dielectric relaxation response.

At the final stage of cure of the D121/DVB reaction (Fig. 4(b)), the very broad dynamic relaxation peak extends from a very low temperature (down to  $-45$  °C) to a very high temperature (higher than the reaction temperature  $70$  °C) as the magnitude of  $\epsilon''$  is still increasing. These observations concerning the distribution of relaxation times in the final stages of cure also suggest that the breadth of the heterogeneity of the D121/DVB network structure is much larger than in D121/St. As will be discussed in Section 3.2.3 and previously reported [13], dynamic mechanical measurements exhibit similar differences in relaxation properties for a cured D121/DVB resin versus the D121/St resin.

### 3.2.2. DSC profile

DSC profiles during the temperature ramp for both systems at different degrees of conversion are shown in Fig. 5(a) and (b). The D121/DVB monomer glass transition is observed at  $-65$  °C. As the conversion increases, the glass transition temperature for monomer/oligomer region shifts to higher

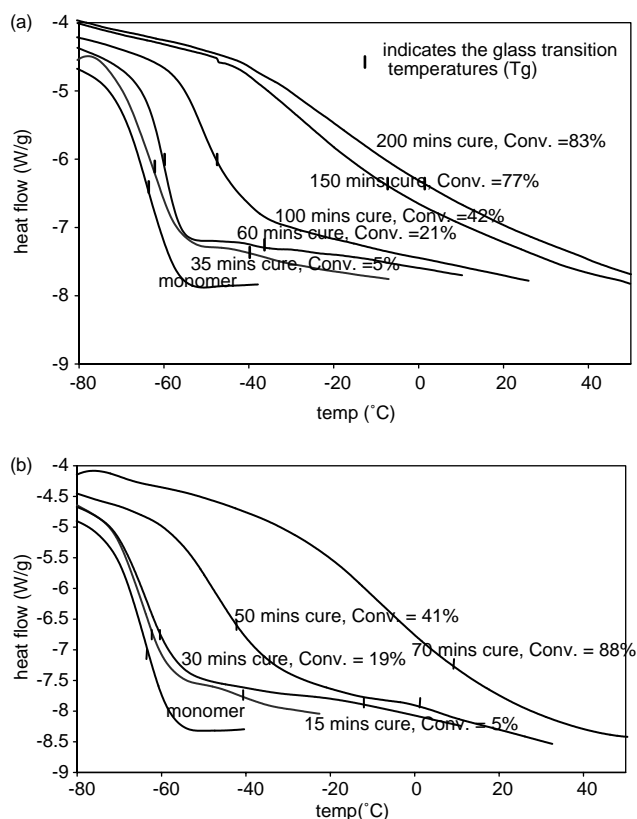


Fig. 5. (a) and (b)  $T_g$  revolution during 70 °C isothermal polymerization of D121/DVB and D121/St.

temperatures, and another weak transition appears at low conversions ( $\alpha=0.05$  and 0.21). While weak due to the initially small fraction of microgels in the total sample, these thermal events occur in the same location on each repetitive run. After that, the monomer/oligomer glass transition merges with the broad glass transition of microgel/microgel clusters to form a very broad transition.

The same trends are observed in the D121/St system (Fig. 5(b)), but the persistence of two glass transitions continues at a higher conversion (after 50 min of cure, 44% conversion). Comparing the 70 °C cured samples for both systems, the D121/DVB has a much broader glass transition than D121/St. This indicates a broader distribution of relaxation times involving cooperative segmental motions and a more heterogeneous network structure during D121/DVB cure. One needs to stress that the D121/St has indeed a broad relaxation spectrum but that the D121/DVB system is even broader. It apparently involves a longer length scale of the boundary and interpenetration of the two regions.

### 3.2.3. Dynamic mechanical properties

Viscoelastic properties of D121/St and D121/DVB systems at different conversions have been characterized in the torsion mode. Fig. 6(a)–(d) shows the evolution of the shear modulus,  $G'$  and  $\tan(\delta)$  as a function of temperature. The dynamic mechanical  $\alpha$ -transition is characterized with the decrease of the shear modulus and the peak of  $\tan(\delta)$  in the dynamic mechanical profiles. As in the dielectric relaxation measure-

ment, the width of the transition reflects the distribution of relaxation times and the existence of two  $\alpha$ -relaxation regions support the existence of a spatial heterogeneity.

For temperatures above  $-50$  °C as seen in Fig. 6(a) and (b), at 54% and to a less clear extent at 20%, two  $\alpha$ -transition peaks in  $\tan \delta$  versus plot are consistent with the existence of the monomer/oligomer region and microgel/polymer region during the reaction. The small loss below  $-50$  °C is due to sub  $T_g$  relaxations as previously shown in the dynamic mechanical spectrum of the D121/St. and D121/DVB systems after curing at 120 °C (Fig. 4; Ref. [13]). The dynamic mechanical measurement was made at a frequency of 2 Hz. The results are shown in Table 3 and support the conclusion that all three measurement techniques are sensing the  $\alpha$ -transition of both the monomer/oligomer and the microgel/polymer regions. It is interesting to note that the magnitude of the loss in the dielectric measurements appears to be proportional to the amount of polar groups in the two regions and two relaxation regions are evident early in the reaction. On the other hand, the magnitude of the two loss peaks in the mechanical spectra are dominated by the mechanical properties of the microgel region. Only when the microgel relaxation moves further away from the monomer relaxation time later in the reaction are the two regions most clearly discerned.

With the advancement of the reaction, the  $\alpha$ -transition of monomer/oligomer region and microgel/polymer region merges and extends to a higher temperature. As seen in Fig. 6(a) and (b), a distinct monomer/oligomer  $\alpha$ -transition peak is no longer observed. Rather a very broad peak, which includes the monomer/oligomer and the microgel/polymer  $\alpha$ -relaxation has increased in width at around 50% conversion for both systems in the dynamic mechanical as well as in the dielectric response. At this point, the relaxation spectrum extends from  $-45$  °C to about 80 °C for the D121/St system and to even higher temperature for the D121/DVB.

In comparing the D121/St and D121/DVB systems, the structure and the functionality of the vinyl comonomer has a stronger influence on the microgel/polymer  $\alpha$ -transition than on the monomer/oligomer region. For D121/St network at 22% conversion (Fig. 6(c)), the microgel/polymer  $\alpha$ -transition begins near  $-40$  °C and extends to 40 °C. The corresponding  $\alpha$ -transition is much flatter and broader when DVB is used as comonomer and begins at  $-40$  °C and extends to 70 °C at this rather low conversion.

For D121/St network with 55% monomer conversion (Fig. 6(d)), a weak broad  $\alpha$ -transition starts around  $-40$  °C and the stronger microgel cluster  $\alpha$ -transition has a peak at 60 °C again reflecting the spatial heterogeneity and breadth of the chain mobility in the network.

For the D121/DVB network with 54% monomer conversion, only one extremely broad  $\alpha$ -transition, which extends from the monomer/oligomer  $\alpha$ -relaxation region through the microgel cluster  $\alpha$ -relaxation region can be observed. This is a result of the more tightly cross-linked network and the larger length scale of the boundary where the two regions interpenetrate each other in the D121/DVB system. The  $\alpha$ -transition of the monomer/oligomer region and microgel/polymer regions have

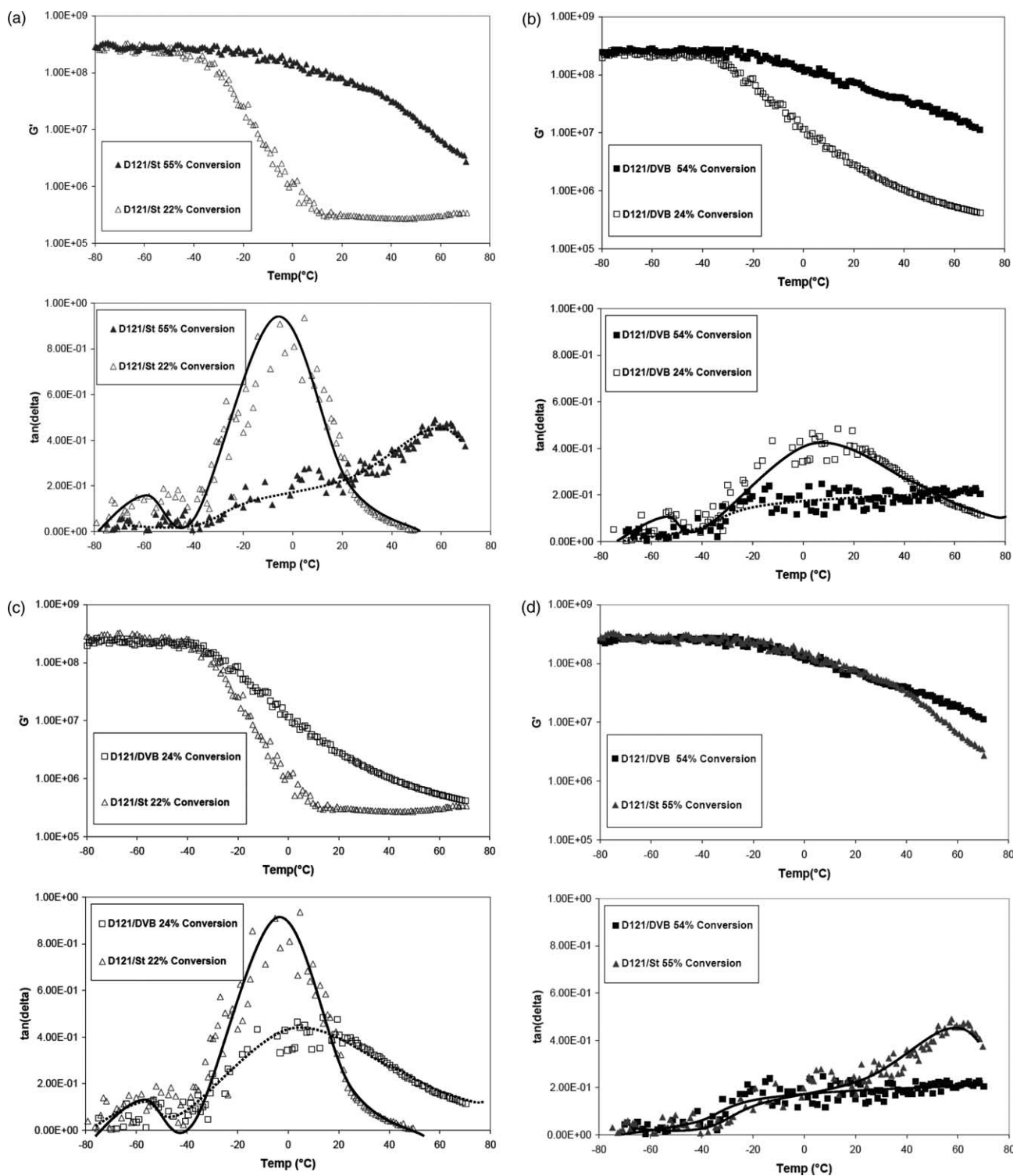


Fig. 6. (a)–(d) Evolution of the storage modulus  $G'$  and  $\tan \delta$  as a function of temperature.

grown into each other and extend to a higher temperature than the curing temperature (70 °C). The magnitude of  $\tan \delta$  is still increasing with temperature as observed in D121/DVB dielectric spectroscopy at this final stage of reaction.

This DMA result supports more spatial heterogeneity in the D121/DVB system as is also indicated by dielectric spectroscopy and DSC profile. This difference is undoubtedly due to the higher functionality of the DVB.

### 3.3. Influence of the comonomer structure and functionality on the network buildup

The comonomer structures have influence on the polymerization rate, network buildup and the system heterogeneity. The use of DVB instead of St increases the mean functionality of the monomer blend and increases the cross-linking density of the microgel network formed. A significant difference

between those two systems is that DVB acts as a cross-linking agent while St acts as a chain extender. This change in comonomer functionality decreases the polymerization rate and increases the heterogeneity of the network structure. It increases the breadth and decreases the sharpness of the boundary between the monomer–oligomer and microgel regions.

#### 4. Conclusion

It is evident from the dielectric, rheometer and DSC results that a spatial heterogeneity develops very early during the polymerization of the dimethacrylate (D121) with both the styrene and the divinylbenzene comonomers. The spatial heterogeneity exists throughout the polymerization but the overlap or interpenetration of each region (monomer/oligomer and the microgel/microgel clusters) into the other increases as the reaction advances. At full cure, an extremely broad frequency–temperature range of relaxation times is created. It represents a very wide range of dynamics extending from the mobility of the short oligomers to the tightly cross-linked microgel clusters.

It is often accepted in the polymer community that the existence of two glass transitions indicates phase separation. Thus, the question does phase separation occur in these systems early during the polymerization? No, not in the conventional sense in which two well defined different compositions exist with the same chemical potential. In that case, a sharp interfacial boundary separates the two chemical compositions. In this chemical homogeneous single-phase system, there exists a spatial heterogeneity. This produces a dynamic heterogeneity observed in the dielectric, mechanical and DSC experiments. There are two distinct regions of differing structure, oligomers and microgels, a point confirmed by dynamic light scattering. There is not a distinct interface between them, rather there is a gradient of interpenetration of one into the other, which is why there is only one phase. What is of particular note is that in the D121/St and the D121/DVB systems, the oligomer and microgel regions are of sufficient

size to exhibit distinctly different glass transitions as detected by DSC. With reaction advancement, the interpenetration of the two regions into each other increases. This creates a spatial heterogeneity encompassing oligomer regions, tightly cross-linked microgel clusters and a very large length scale of overlap and interpenetration of each into the other. Finally, we note this result provides additional evidence that the existence of two  $T_g$ 's does not by itself indicate a two-phase system.

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