Reaction Kinetics and Morphological Changes during Isothermal Cure of Vinyl/Dimethacrylate Networks

L. Rey,* J. Galy, and H. Sautereau

Laboratoire des Matériaux Macromoléculaires UMR 5627, Institut National des Sciences Appliquées, Bât. 403, 20, avenue Albert Einstein, 69621 Villeurbanne Cedex, France

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ABSTRACT: Free radical polymerization of two formulations based on tetraethoxylated bisphenol A dimethacrylate initiated by azobis(methylbutyronitrile) were investigated. Two comonomers were used (20 wt %), styrene or divinylbenzene. The polymerization was conducted under isothermal conditions at various temperatures between 60 and 80 °C. The influence of comonomer structure and cure temperature is discussed and focused on two main points: reaction kinetics, i.e., evolution of double bonds, and radical concentration and morphological changes during the course of polymerization. The use of DVB as comonomer enhances diffusion limitation. The polymerization rate and the double-bond conversion are also limited when DVB is used, even at higher cure temperature where diffusion is enhanced. The formation of microgels was followed by dynamic light scattering. Microgels that have diameters of between 19 and 40 nm tend to aggregate into clusters up to the gel point where a macroscopic network is formed. Clusters are bigger when DVB is used because of the large amount of pendant double bonds. At the gel point, the final morphology of the network is fixed and consists of the agglomeration of single microgels which were observed by atomic force microscopy. With an increase in cure temperature, microgels and clusters are found to be smaller in both systems.

Introduction

Free-radical bulk polymerization of multifunctional monomers is one of the most efficient methods of synthesizing a highly cross-linked polymer with high mechanical properties. The network formation process in free radical polymerization is quite different from that in step growth polymerization. One of the most important characteristics of such highly cross-linked network formation is the spatial heterogeneity in the reacting system. The formation of microgels in the early stage of the polymerization is the primary cause of structural heterogeneity in the network. Microgels are densely cross-linked, and cycled polymers and result from the formation of highly cross-linked regions near the site of the initiated radical. As a consequence, from the beginning of the reaction, polymerization is diffusion-controlled, and the autoacceleration in the polymerization rate is enhanced.[1−6]

The presence of microgels also strongly affects the polymerization mechanism and kinetics. Several phenomena such as reaction kinetics, rheological change, and microstructure formation control the final properties of the resulting network. The objective of this work is, therefore, to describe the buildup of two different dimethacrylate-based networks. The influence of the cure temperature and the comonomer structure will be investigated.

Materials

Two systems were used in this study and were based on tetraethoxylated bisphenol A dimethacrylate (D121) from Akzo-Nobel (80 wt %) and two comonomers (20 wt %), styrene (Aldrich) or divinylbenzene (Fluka). A chain transfer agent, 1-dodecanethiol, was also used (0.5 phr). Azobis(methylbutyronitrile) (AMBN) was used as an initiator (0.2 phr). All products were used as received; their chemical structures are shown in Table 1. The two formulations will be called D121/ST or D121/DVB as a function of the comonomer used. The systems used are different because of the comonomer structure (ST or DVB). As a consequence, the mean functionality (f) and the initial double-bond concentration vary between the two systems: f is equal to 3.8 and 2.9 for the D121/DVB and D121/ST systems, respectively, and the initial total double-bond concentration is equal to 5.67×10^{-3} and 4.84×10^{-3} mol/g for the D121/DVB and D121/ST systems, respectively.

The mixing was carried out in a glass vial with a magnetic stirrer at ambient temperature for 20 min to ensure a homogeneous blend of all components. The blend was flushed with nitrogen under agitation to remove oxygen in order to avoid inhibition. Then the reactive liquid was introduced into a mold made of two glass plates separated by a 2 mm thick silicone gasket. The cross-linking reaction was conducted under isothermal conditions in a temperature-controlled water bath.

Experimental Section

Rheological Measurements. A torsional dynamic mechanical analyzer (Rheometrics RDAII dynamic mechanical analyzer) was used to detect gelation during the isothermal cure; 40 mm diameter aluminum plates were used. The storage G' and loss G'' modulus were measured at regular intervals, at 10 rad s^{-1}, at zero normal force, and the strain was maintained constant at 10%. In a typical experiment, the liquid monomer was applied between the plates of the rheometer and the distance set to 2 mm. The temperature was maintained constant using a nitrogen forced gas flow. The usual way to determine the exact gel point from rheological data involves finding the time at which tan δ becomes independent of frequency.[7,8] This criterion can be applied if the evolution of tan δ is slow during each measurement. In our case, the transition is so fast that not enough data are available to determine a precise gel point by this method. The rise in G' is another criterion of the liquid−gel transition for a cross-linking polymer. The gel point was determined as the time at which G' reaches the value of 1 Pa. Considering that the rise in G' is

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* To whom correspondence should be addressed.

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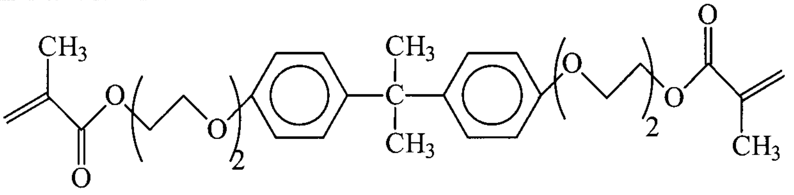
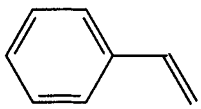
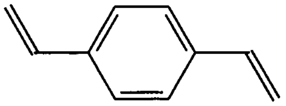
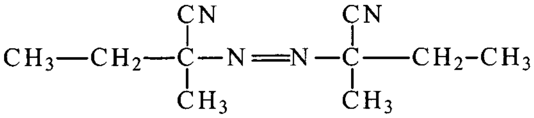
Table 1. Chemical Products Used in Synthesis of Materials

Name	*Chemical Formula*
Dimethacrylate of tetraethoxylated bisphenol A (D121®) *Akzo-Nobel*	 stabilized by 100-200 ppm of p-methoxyphenol
Styrene (ST) *Aldrich*	 purity: 99.7% stabilized by 10-15 ppm of terbutylcatechol
Divinylbenzene (DVB) *Fluka*	80% mixture of p- and m isomers 16% of ethylvinylbenzene 1.5% of diethylbenzene 0.5% of naphthalene  stabilized by 900-1090 ppm of terbutylcatechol
1-Dodecanethiol *Aldrich*	$CH_3(CH_2)_{11}SH$ purity: 98%
Azobis methyl butyronitrile Vazo 67® (AMBN) *Dupont*	 $CH_3-CH_2-C(CN)(CH_3)-N{=}N-C(CN)(CH_3)-CH_2-CH_3$ purity: 98%

very dramatic, this criterion is efficient, and the error concerning the gel time is less than 1 min.

Reaction Kinetics. A differential scanning calorimeter (Perkin-Elmer DSC-7) was used to measure the heat of polymerization during the isothermal cure. In all studies, about 20 mg of monomer blend was weighed in order to fill the aluminum pan to avoid oxygen inhibition. The instrument was calibrated with indium. The runs were ended when there was no further exotherm. The rate of heat release ($d\Delta H_t/dt$) measured by DSC can be directly converted into the overall reaction rate ($d\alpha/dt$) as a function of time using the following formula:[9]

$$d\alpha/dt = 1/\Delta H_T(d\Delta H_t/dt) \qquad (1)$$

where ΔH_T is the total heat of reaction. ΔH_T was calculated from theoretical values for methacrylate and vinyl double bond reactions.[10-13]

$$\Delta H_{D121/ST} = 311 \text{ J/g}, \quad \Delta H_{D121/DVB} = 353 \text{ J/g}$$

Double-Bond Conversion Measurement. The double-bond conversion was measured in situ by transmission near-infrared spectroscopy using a specific device described elsewhere.[14] The temperature was controlled all along the cure with a thermocouple (K type) directly plunged in the reactive mixture to ensure that isothermal conditions are respected. Fourier transform infrared spectroscopy was performed using a Nicolet Magna-IR 550 spectrometer. An Ever-GloTM source was used along with a KBr beam splitter on a DTGS-KBr detector. During the isothermal reaction, the spectrum at each time interval represents the sum of 32 individual scans with a resolution of 4 cm^{-1}. The two absorption bands at 6166 and 6135 cm^{-1} have been used to follow methacrylate and vinyl double-bond concentration. The spectra were deconvoluted using XPSPeak software. The peak area was used for calculations taking into account the molar absorption coefficient of each type of double bond.

Radical Concentration. Radical concentration was measured in situ by electron spin resonance (ESR) during the isothermal cure to avoid the possible change of radical concentration during quenching. Sealed quartz ampules with a 3 mm diameter containing the reactive mixture were inserted into the cavity of a Varian E9 spectrometer (9.3 GHz X band) or Bruker ER300D. The reaction temperature was controlled with a gas flow to ensure isothermal conditions. Spectra were recorded as a function of reaction time to follow the polymerization in detail. Radical concentration was determined by double integration of the observed ESR spectrum which is the first derivative of the absorption spectrum. The absolute radical concentration was obtained after calibration with a stable free radical source (Pitch).

Particle Size. A dynamic light scattering (DLS) goniometer (Brookhaven BI-8000) with a digital correlator was used to measure the particle size of partially reacted samples before gelation. The samples were diluted in dichloromethane. A Spectra Physics S 2000 laser system with an output power between 50 and 600 mW and a wavelength of 514 nm was used

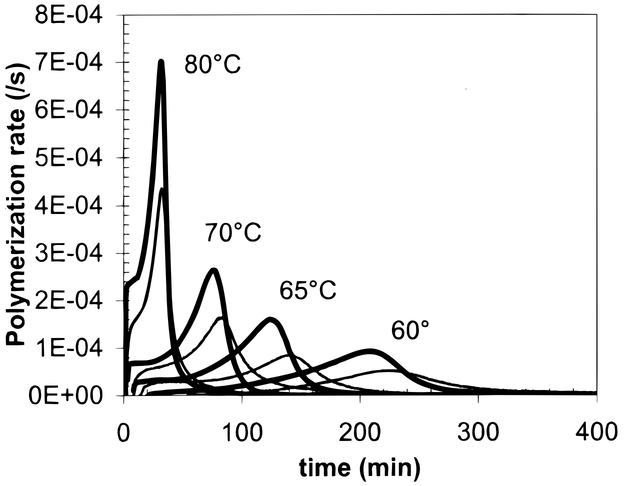


Figure 1. Evolution of the polymerization rate as a function of time at different isothermal cure temperatures for D121/ST (—) and D121/DVB (−).

Table 2. Gel Times (min) for D121/ST and D121/DVB during Isothermal Cure between 60 and 80 °C

	temp (°C)				
	80	75	70	65	60
D121/ST	12	19	27	41	62
D121/DVB	17	25	36	56	102

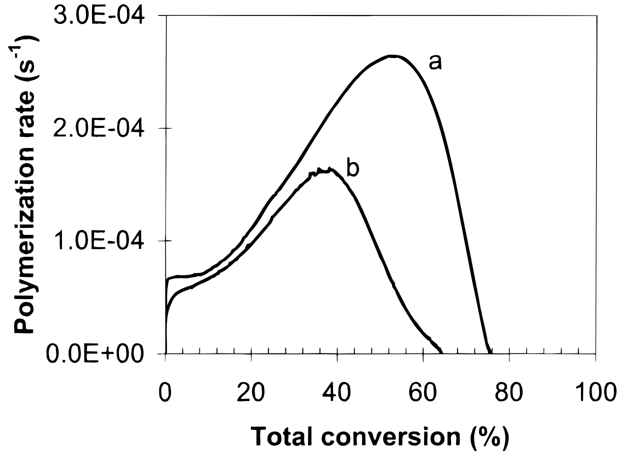


Figure 2. Polymerization rate versus conversion for D121/ST (a) and D121/DVB (b) during isothermal treatment at 70 °C.

as the light source. Measurements were made with a sample time of 1 μs. The measuring angle was fixed at 90° for all tests. The fluctuations of the scattered intensity are related to the particle sizes of particles. The nonnegative linear square function was used as a correlation function to calculate the distribution of particle diameters.

Microstructure Study. Atomic force microscopy (AFM; Digital Instrument Nanoscope 3A) was used in tapping mode to observe the topology of fracture surface. Samples were razor blade notched and fractured at room temperature in order to create a mirrorlike surface suitable for AFM observations. The tip used was 2 μm high with a top half angle of 17°.

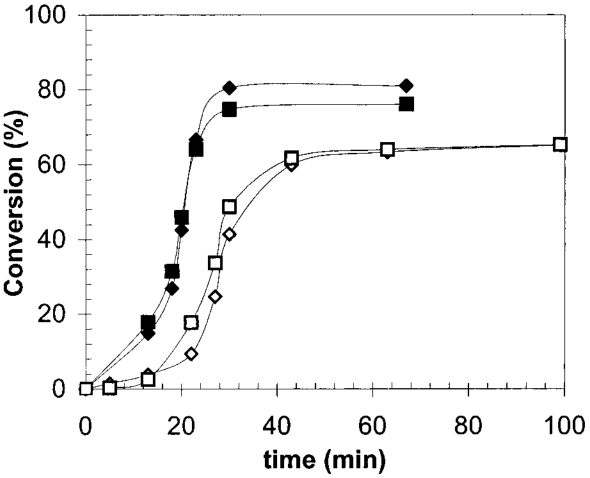


Figure 3. Vinyl (squares) and methacrylate (diamond) double-bond conversion during isothermal cure at 80 °C for D121/ST (full symbol) and D121/DVB (empty symbol).

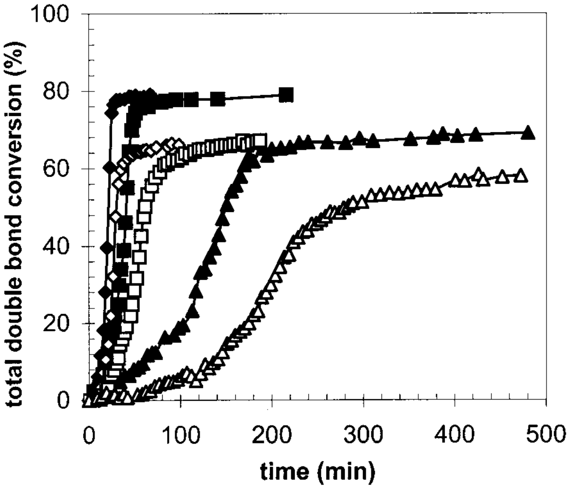


Figure 4. Total double-bond conversion during isothermal cure at 80 °C (◆), 70 °C (■), and 60 °C (▲) for D121/ST (full symbol) and D121/DVB (empty symbol).

Results

Gelation. The gel times measured by RDAII for each formulation at different cure temperatures are reported in Table 2. For the same temperature, the gel time is always longer for D121/DVB compared to D121/ST. This is an unexpected result as it is well-known that as the amount of multifunctional monomer increases (use of DVB instead of ST), the gel time should decrease.[4,11] In this case the amount of inhibitor in vinyl monomers is very different between ST and DVB and explains the shift of D121/DVB gel time to higher value. As expected, the gel time decreases as the cure temperature increases.

Kinetics. Figure 1 shows the isothermal DSC profiles of polymerization rate for D121/ST and D121/DVB at different cure temperatures between 60 and 80 °C. The total heat of reaction calculated from DSC data, ΔH_{iso}, and the maximum polymerization rate, R_{pmax}, are reported in Table 3. In Figure 2, the rate of polymerization is plotted as a function of conversion calculated from theoretical values of the total reaction heat.

The induction times, t_{ini}, reported in Table 3 show that the D121/ST system starts reacting faster than the D121/DVB system. As discussed previously, the difference in inhibitor content in ST or DVB reported in Table 1 explains those results.

Double-Bond Conversion. The vinyl and methacrylate double-bond conversion obtained after deconvolution of the IR spectrum is represented in Figure 3 for an isothermal curing temperature of 80 °C (Figure 3). The total double-bond conversion during D121/ST and D121/DVB polymerization is plotted in Figure 4 for three isothermal cure temperatures: 60, 70, and 80 °C.

Table 3. Results from DSC Analysis during Isothermal Cure

	D121/ST				D121/DVB			
temp (°C)	80	70	65	60	80	70	65	60
ΔH_{iso} (J g^{-1})	296	235	211	189	242	227	172	149
ΔH_{iso} (kJ/mol C=C)	61.2	48.6	43.6	39	42.7	40	30.3	26.3
t_{ini} (min)	1.2	3.4	8.6	21	1.4	5.9	13.8	51
R_{pmax} (s^{-1})	6.9×10^{-4}	2.6×10^{-4}	1.6×10^{-4}	0.9×10^{-4}	4.3×10^{-4}	1.5×10^{-4}	0.8×10^{-4}	0.5×10^{-4}

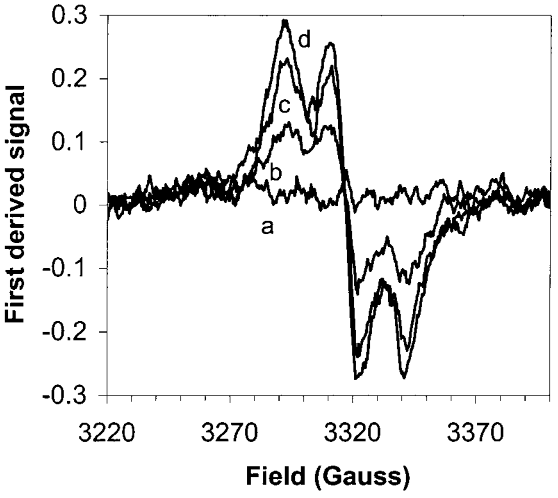


Figure 5. Samples of ESR spectra during isothermal polymerization of D121/DVB at 86 °C: (a) 0 min, (b) 19 min, (c) 23 min, and (d) 51 min.

Table 4. Rate Constant k_{12} for Radical Monomer Reaction at 60 °C (L mol^{-1} s^{-1})[18]

	ST radical	MMA
ST monomer	165	1130
MMA monomer	314	575

Radical Concentration. Typical ESR spectra observed during D121/DVB polymerization are given in Figure 5. Two types of radicals are formed during D121/ST and D121/DVB polymerization. On one hand, methacrylate radicals exhibit a 13-line ESR spectrum in a liquid state and a nine-line ESR spectrum in the solid state.[4] On the other hand, the polystyryl radical has a three-line shape ESR spectrum.[15−17]

From Figure 5 it can be observed that only trapped styryl radicals and no methacrylate radicals have been detected during the cure of D121/DVB system. The in-situ ESR measurement is an instantaneous equilibrium between radicals that are created by the decomposition of AMBN and radicals that recombine. Therefore, the more stable radicals or the statistically more probable radicals can be easily detected.

The values of the rate constant k_{12} for a radical monomer reaction given in the literature[18] are reported in Table 4. They show that a styryl radical reacts at a lower rate than a methacrylate one. Styryl and methacrylate radicals are present in the reacting system, but styryl radicals are in higher concentration than the methacrylate radicals that react very rapidly and therefore could not be detected.

The instantaneous radical concentration during D121/ST polymerization was not high enough to be measured because it was probably below the detection limit of the ESR spectrometer used in this study which is close to 5×10^{-4} mol L^{-1}. The evolution of the radical concentration in D121/DVB system as a function of time for three different temperatures is reported in Figure 6.

Microgel Size. The sizes of the primary polymer or microgel resulting from the analysis by DLS of partially reacted samples of D121/ST and D121/DVB are reported in Table 5. As described by Dusek,[1−3] microgels, compact and internally cross-linked molecules, are formed in the early stage of polymerization. Three distributions of particles are observed: the first population of diameter, D_1, smaller than 10 nm can be attributed to small macromolecules or “native microgels”. The second distribution of diameter, D_2, ranging from 10 to 40 nm can be considered as single microgels and are of the same order of magnitude as those measured by Chiu et al.[10,11] (average diameter ranged from 12 to 18 nm for microgels) during EGDMA polymerization at 60 °C using the same technique. The third distribution of diameter, D_3, ranges from 40 up to 400 nm and may be considered as clusters.

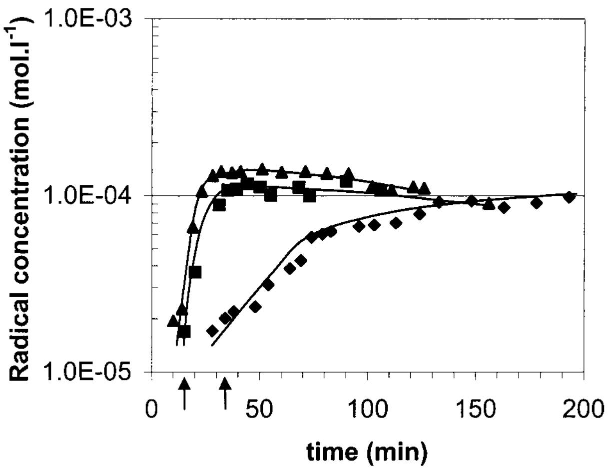
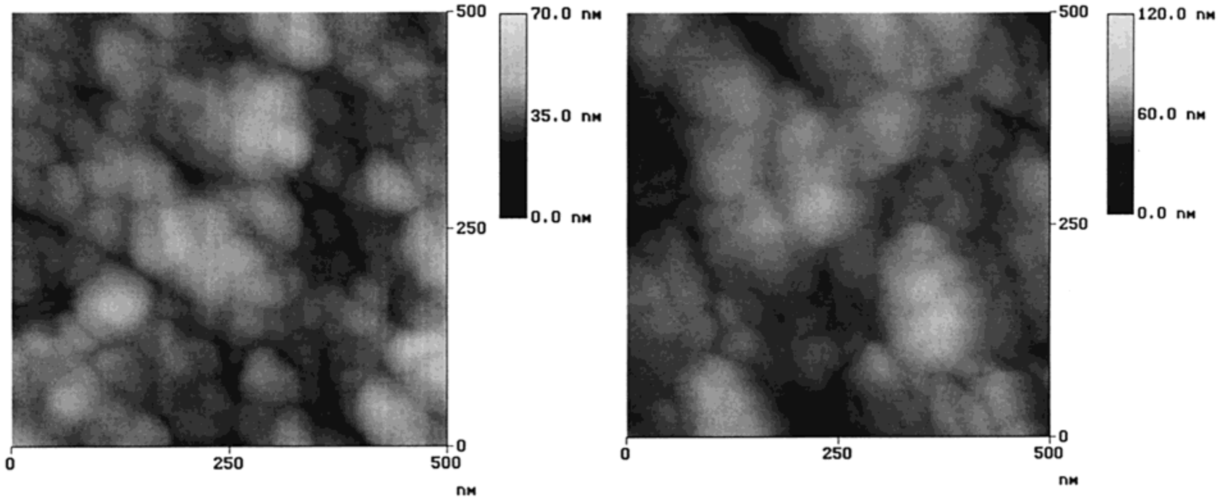


Figure 6. Evolution of styryl radical concentration for D121/DVB during isothermal cure at 70 °C (◆), 80 °C (■), and 86 °C (▲). Arrows indicate the gel time.

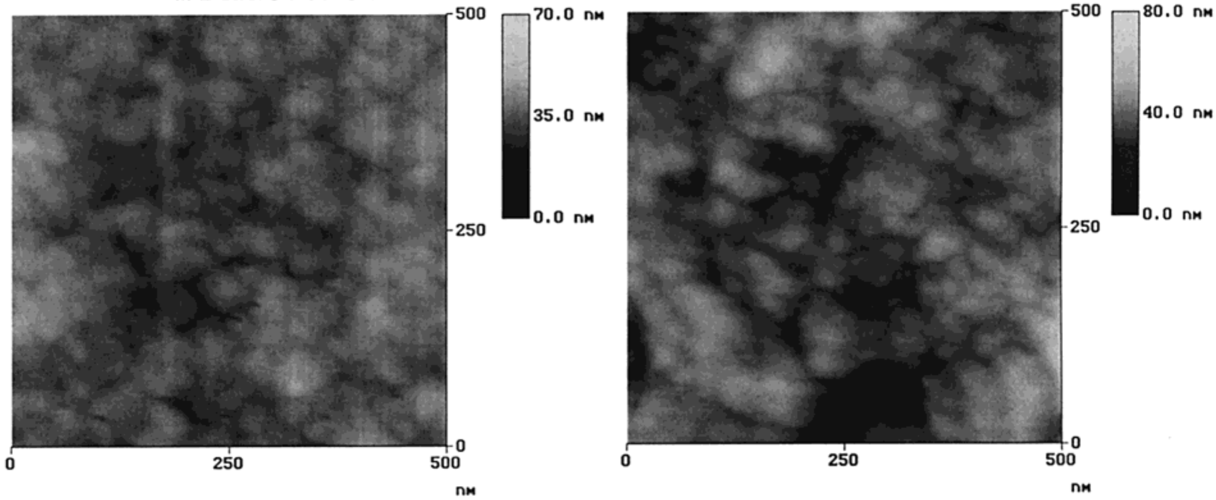
Microstructure. Fracture surfaces shown in Figure 7 for both systems exhibit a nodular structure. The nodular structure is a consequence of the network buildup through the formation of microgels and their growth into clusters. Fractures in such brittle materials occur by cracks propagating via points of lowest strength[19] or lowest cross-linking density. In dimethacrylate-based networks the weakest region is situated around the microgels that are strongly cross-linked. Nodules can also be attributed to microgels or clusters of microgels.

Discussion

Network Buildup during Isothermal Polymerization of the D121/DVB System. Radical polymerization of multifunctional monomers such as D121 or DVB is currently described as a heterogeneous process because of microgel formation during reaction. Shortly after the beginning of the reaction, microgels can be detected by DLS as reported in Table 5. The increase of particle diameter as a function of time can be explained by microgel agglomeration. The pendant double bonds in the microgel core cannot take part in further reactions, but peripheral pendant double bonds



a. D121/ST 60°C cured b. D121/DVB 60°C cured



c. D121/ST 80°C cured d. D121/DVB 80°C cured

Figure 7. The 500 nm × 500 nm fracture surface of D121/ST and D121/DVB cured at 60 and 80 °C.

Table 5. Results of DLS Measurements at 60 °C; Percentage Indicates the Repartition of Particle Diameters in Each Population When the Distribution Is Bi- or Trimodal[a]

time (min)	conv,[b] %	D, nm	D_1, nm	V_1, %	D_2, nm	V_2, %	D_3, nm	V_3, %
				D121/ST				
15	0.75	8			6–12	100		
25	2	9			9–18	100		
35	3	13			13–27	100		
40	4.2	18	8–12	54	23–35	46		
45	4.8	23	7–9	37	24–31	63		
50	5.2	33	4–6	15	14–25	46	44–92	39
60 (gel 62 min)	6.1	53	3–4	15	19–40	47	75–158	38
				D121/DVB				
30	1	8	2–4	42	8–12	58		
40	1.4	8	1–2	33	9–16	67		
50	1.5	11	3–4	38	12–24	62		
60	2	17	5–9	56	21–38	44		
70	3.5	22	3–5	17	19–39	83		
80	4	25	6–14	37	25–44	63		
90	4.8	48	4–6	12	16–29	41	60–107	47
100 (gel 102 min)	6	70	3–14	49	22–90	42	238–355	9

[a] D = average particle size; D_1, D_2, D_3 = particle sizes of native microgels, microgels, and clusters of microgels, respectively; V_1, V_2, V_3 = the respective volume fractions. [b] Conversions are calculated using near-infrared spectroscopy.

participate in structure growth by interparticular reaction to form aggregates.[1–3,20] As the polymerization progresses, large microgel clusters (diameters ranging from 20 to 355 nm) are formed, and particle size distribution becomes bi- and trimodal.[10,11,15–17]

The polymerization rate measured by DSC is strongly affected by the heterogeneous formation of the network. At very low conversion, the reaction passed from chemical control to diffusion control leading to an evolution of the rate of polymerization, i.e., autoacceleration or gel effect: growing radicals linked to the three-dimensional network have a restricted mobility, and the termination rate decreases so it increases the polymerization rate. The gel effect begins at about 3% of

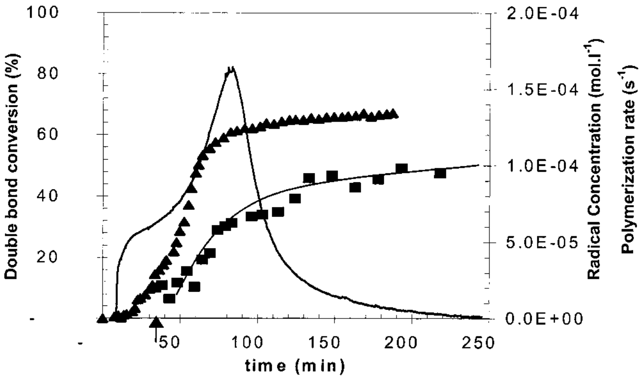


Figure 8. Radical concentration (■), total double-bond conversion (▲), and polymerization rate (−) during isothermal cure at 70 °C of D121/DVB. Arrow indicates the gel time.

double-bond conversion during the D121/DVB polymerization at 70 °C (Figure 2).

The gel time, as measured by a dynamic rheological test, corresponds to the onset of formation of macroscopic gel. The gel time corresponds to the transition from a dispersion of microgels in a monomer blend a macrogel swelled by a monomer blend. Gelation occurs for a double-bond conversion close to 12%. The gel effect is enhanced, leading to an acceleration of the polymerization rate. The trapping of growing radical in the network becomes more and more efficient, and the radical concentration measured by ESR starts increasing (Figure 6).

As the polymerization proceeds, the environment becomes more and more restricted, and the propagation reaction also becomes diffusion limited. The rate of polymerization decreases when both propagation and termination reactions are limited by the low ability of the reactive species to diffuse. In the same period of time, the radical concentration reaches a stable value. The growing radicals are trapped in a glassy matrix and cannot take part in further termination or propagation reaction.

The double-bond reactivity is also affected by microgel formation. Pendant double bonds have a low reactivity because of steric hindrance.[21] What is more, in the case of DVB, it is well-known that the pendant double bond is half as reactive as the monomer one.[22] Trapped double bonds cannot take part in further reactions so the final conversion is always incomplete whatever the cure temperature (Figure 4). This trapping could be labeled as a pseudotermination by shielding.

On the basis of these results, the curing process of the dimethacrylate/vinyl-based network can be described from Figure 8 into four steps: induction period, microgel formation and agglomeration, gelation, and postgelation.

1, 2. After an induction period where inhibitors are consumed polymerization begins, and the conversion starts to increase.

3. Gelation occurs when microgels have grown and connected into clusters, resulting in a macroscopic network in which about 90% of the double bonds remain unreacted. At this stage of the curing process, the mobility of the reacting system decreases rapidly; termination reactions are more and more diffusion-controlled. Thus, the polymerization rate increases due to autoacceleration.

4. Finally macrovitrification occurs, leading to a decrease in the polymerization rate, i.e., autodeceleration. Macrovitrification is the direct consequence of progressive microvitrification of the inaccessible microgel core throughout the polymerization process as described by Lange et al.[23] Termination and also propagation reactions are diffusion-limited. Therefore, residual monomers, double bonds, and radicals stay trapped in the network.

Influence of the Comonomer Structure on the Network Buildup. The use of styrene instead of DVB decreases the mean functionality of the monomer blend and decreases the cross-linking density of the network formed. The main difference between those two systems is that DVB acts as a cross-link agent when ST acts as a chain extender. So, the change in comonomer functionality strongly affects the polymerization kinetics and the structure of the network formed.

Figure 2 shows the difference in the polymerization rate between D121/ST and D121/DVB systems during an isothermal cure at 70 °C. The reaction rate is always higher when ST is used. The presence of DVB has a complex influence on the polymerization rate. On one hand, the additional cross-linking facilitates the gel effect leading to an increase of the polymerization rate. On the other hand, the propagation rate is also influenced by the ability of reactive species to diffuse. Thus, because the D121/DVB system generates a higher cross-linked structure, the polymerization rate is limited and lower than the D121/ST one. As a result, the maximum polymerization rate occurs at a higher conversion for the D121/ST system (54%) compared to D121/DVB systems (37%). The reactive species mobility is restricted more rapidly in the more cross-linked D121/DVB network. Cook[12] obtained similar results: he showed that the maximum polymerization rate decreases with the decreasing size of the spacer group (*n*) in *n*-ethoxylated bisphenol A dimethacrylate photopolymerization.

This evolution is confirmed by ESR experiments. The radical concentration is not high enough to be detected during D121/ST polymerization. Radical trapping is less effective during D121/ST polymerization because of the higher mobility of radicals in the reacting system.

During an isothermal cure, NIR measurements show no difference between vinyl and methacrylate double-bond conversions for the same system (Figure 3). However, it is interesting to note that the rate of methacrylate double-bond consumption depends on the comonomer used and is higher in the D121/ST system. This result is consistent with DSC results which show that the use of ST increases the polymerization rate. The isothermal heat of reaction at the end of the isothermal cure reported in Table 3 is always lower for the D121/DVB system, proving that more double bonds and radicals are trapped in the network. For the same cure temperature, the total double-bond conversion is also always lower for the D121/DVB system (Figure 4).

The microgel sizes before gelation reported in Table 5 are not very different when considering the D121/ST or the D121/DVB system at the beginning of polymerization. However, just before gelation, the last DLS measurements show bigger clusters for the D121/DVB system. The high level of pendant double bond in the D121/DVB system facilitates the intermicrogel reaction creating big clusters. These results are consistent with those of Nagash et al.,[24] who found that the increase of EGDMA content in MMA/EGDMA copolymerization results in a higher cluster content.

The 60 °C-cured sample surfaces observed by AFM (Figure 7) can be compared with the DLS results (Table 5). Nodules in a 60 °C-cured D121/ST surface have a diameter of the order of 30 nm when DLS measurements show that single microgels have a diameter, D_2, between 19 and 40 nm just before gelation. Bigger nonspherical nodules which have a diameter of the order of 80 nm can be compared with the biggest population of microgel clusters which have a diameter, D_3, between 75 and 158 nm by DLS measurement. The same comparison can be made with a 60 °C-cured D121/DVB surface, and DLS results just before gelation. Small nodules (30−70 nm) can be compared with a single microgel (22−90 nm) in DLS measurement when big clusters (220 nm), having a raspberry aspect can be related to the population 3 (238−355 nm) from DLS.

Therefore, the development of microgels, their agglomeration into clusters, and their percolation at the gel time determine the final network morphology as shown by AFM at the end of the cure.

Influence of the Cure Temperature on the Network Buildup. Because reaction kinetics is governed by diffusion, the cure temperature is one of the main parameters that control the network buildup. By increasing the cure temperature, reactive species have higher energy to break the diffusion limitation and vitrification is delayed. The reaction rate and the total heat of polymerization from DSC results (Table 3) and the double-bond conversion (Figure 3) increase with the cure temperature.

Because the reaction is thermally initiated by AMBN, a higher cure temperature leads to a higher concentration of growing radicals. As a consequence, more radicals are trapped at the gel time as shown in Figure 6. If the temperature is high enough (86 °C), trapped radicals are able to diffuse across the network to terminate, and the radical concentration can decrease.

It is interesting to note from NIR results that the total double-bond conversion never reaches the value of 100% even at a high cure temperature. This result is in agreement with the observation that the total heats of polymerization, ΔH_{iso}, measured by DSC are always lower than the theoretical heat of polymerization. There is a maximum conversion of 65% for the D121/DVB system and 80% for the D121/ST system. Even at high temperature where diffusion is easiest, an amount of double bonds, terminated by occlusion, stays trapped in the network. This amount cannot be reduced by using a higher cure temperature and depends on the monomer used or in the structure of the network formed.

When the cure temperature increases, microgels and clusters formed are smaller in both systems, as shown in Figure 7c,d. Ziaee and Palmese[25] describe similar effects on vinyl ester network morphology. They show that the nodule size formed in a 30 °C-cured vinyl ester is larger than that of 90 °C-cured vinyl ester.

Conclusion

The reaction kinetics and morphology in dimethacrylate-based networks are strongly affected by the cure temperature and the comonomer structure. Early in the reaction, polymerization passes from chemical control to diffusion control so that the final conversion, the polymerization rate, and the reacting network structure depend only on the network mobility and hence on the temperature and monomer structure.

The use of DVB as comonomer increases diffusion limitation and limits the final conversion and the polymerization rate. The network generated from the D121/DVB system is strongly cross-linked, and a large amount of double bonds and radicals stay trapped in the network. Dynamic light scattering shows that single microgels tend to aggregate into clusters to form a macroscopic network. The amount of pendant double bond is larger when DVB is used, resulting in higher microgel agglomeration by interparticular reaction. A comparison can be made between microgel diameters measured just before the gel point by DLS and those observed by atomic force microscopy at the end of the isothermal cure.

Increasing the cure temperature increases the polymerization rate and the amount of trapped radicals. Microgel and cluster diameters decrease. There is not a large difference between conversion after isothermal cure at 80 and 70 °C. In this case the temperature is high enough to ensure good mobility of the reactive species, and the final conversion depends on monomer structure. For lower temperatures, diffusion limitation is enhanced, and the final conversion is limited.

Further works will concern mechanical and viscoelastic properties and the fracture behavior of those networks.

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