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Free-radical crosslinking polymerization of neopentyl glycol dimethacrylate in the presence of lauryl mercaptan

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Abstract

Neopentyl glycol dimethacrylate was polymerized in bulk in the presence of lauryl mercaptan as a chain transfer agent, the primary chain length being reduced to a comparable order in allyl polymerization, and the gelation behavior was compared with diallyl terephthalate (DAT) polymerization as a typical example of multiallyl polymerizations. No Trommsdorff effect was observed, even beyond the gel point conversion, in spite of the polymerization of divinyl monomer, as were the cases of the bulk polymerization of multiallyl compounds. The variation of molecular weight distribution curves with conversion was quite similar to DAT polymerization. The deviation of actual gel point from the theoretical one was also similar. Moreover, the swelling ratio of the gel obtained just beyond the gel point was very high. Thus, no substantial difference was observed between allyl and vinyl polymerizations in the case where the primary chain lengths were adjusted to be comparable. In addition, no microgelation occurred up to the gel point. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

We have been concerned with the network formation in the free-radical crosslinking polymerization and copolymerization of multivinyl compounds, especially including diallyl esters and dimethacrylates, by focusing our attention on the mechanistic discussion on the deviation from Flory–Stockmayer's theory ([1] and references cited therein); first, the reasons for the greatly delayed gelation in diallyl polymerizations were discussed mechanistically in detail and then the discussion was satisfactorily extended to a detailed understanding of the network formation in common multivinyl polymerizations. Thus the striking feature of diallyl polymerization was the fact that no microgelation was observed during the polymerization until the gel point conversion in the bulk polymerization of diallyl phthalate (DAP) [2], as completely opposed to the cases where numerous reports on microgel formation were published in the homopolymerizations of multivinyl compounds and their copolymerizations with monovinyl monomers [3–8]. This finding is important since microgelation leads not only to delayed gelation, but also to the inhomogeneity of network structures of three-dimensional polymers as closely related to their properties.

In this connection, the most significant difference between allyl and vinyl polymerizations is in the length of their primary chains which has a predominant influence on gelation, since in the allyl polymerization an occurrence of monomer chain transfer, i.e. a well-known degradative chain transfer [9] as an allylic hydrogen abstraction reaction of growing polymer radical from monomer to give a resonance-stabilized allyl radical, is quite remarkable and only the oligomer is formed. Therefore, we tried to carry out the oligomerization of neopentyl glycol dimethacrylate (NPGDMA), a sparingly cyclopolymerizable divinyl monomer, in the presence of lauryl mercaptan (LM), a chain transfer agent, in order to reduce the primary chain length down to a comparable order in allyl polymerization; otherwise, a direct comparison of both diallyl and divinyl polymerizations cannot be made easily since we do not have an alternative way of enlarging the primary chain length in the allyl polymerization. Here diallyl terephthalate (DAT) was polymerized for comparison. Certainly, the aim of this study would be to remove the obstacles in allyl and vinyl polymerizations for the discussion of the mechanisms of network formation in the crosslinking polymerization of multivinyl compounds.

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2. Experimental

NPGDMA and 1,6-hexanediol dimethacrylate (HDMA), supplied by Kyoeisha Chemical Co., Ltd., and DAT, supplied by Daiso Co., Ltd. (monomers), and 1,1′-azobiscyclohexane-1-carbonitrile (ACHCN) and benzoyl peroxide (BPO) (initiators) were purified by conventional methods as described previously [10]. LM as chain transfer agent (extra pure reagent) was used as commercially available.

Polymerization was carried out as described previously [11]. After a predetermined time of reaction, the polymer was precipitated by pouring the reaction mixture into a large excess of chilled methanol containing a small amount of hydroquinone as inhibitor. The gel fraction of polymer at conversions beyond the gel point was obtained by extracting the sol fraction with tetrahydrofuran.

The weight-average molecular weight, $\overline{M}_w$, and molecular-weight distribution were measured by size-exclusion chromatography (SEC) using a dual detector system, set in the direction of flow, consisting of a multi-angle laser light scattering (MALLS) device and a differential refractometer in sequence. SEC-MALLS measurements were carried out at 40°C in tetrahydrofuran using a Shodex GPC KF-806L × 5 columns, at polymer concentrations 0.1–0.5% (w/v) and flow rate 1 ml/min. The MALLS device was a DAWN Model F (Wyatt Technology Corp.) where the laser beam, of wavelength 632.8 nm, was focused on a 67 μl flow cell.

3. Results and discussion

3.1. No observation of Trommsdorff effect

Bulk polymerization of NPGDMA was conducted under the following conditions: [LM]/[NPGDMA] = 1/10 (by mole); [ACHCN] = 0.01 mol/l; 50°C. Fig. 1 shows the conversion–time curve, together with the percentage of gel polymer obtained by the sol–gel separation. No Trommsdorff effect [12] was observed, even beyond the gel point conversion as were the cases of the bulk polymerization of multiallyl compounds [2,10,13]. Of course, in the polymerization of multiallyl compounds, this is ascribed to chain transfer from the growing polymer radical to the monomer [9]. That is, the degradative chain transfer is essentially the termination reaction of growing polymer radical to form a dead polymer, thus acting to keep the primary chain length constant; this is an important fact for our mechanistic discussion of the network formation in the free-radical crosslinking polymerization and copolymerization of multivinyl compounds because the primary chain length is expected to contribute significantly to the gelation by theory [14].

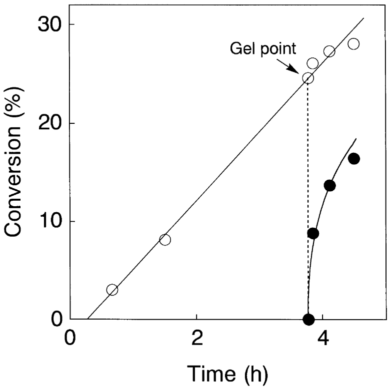

Fig. 1. Conversion–time curve for the polymerization of NPGDMA in the presence of LM ([LM]/[NPGDMA] = 1/10). Polymerization was conducted in bulk using 0.01 mol/l of ACHCN at 50°C. Open and full symbols correspond to total and gel polymers, respectively.

In this connection, the chain transfer reaction of the growing polymer radical to LM would play an important role for keeping the primary chain length constant in the bulk polymerization of NPGDMA in the presence of LM as chain transfer agent.

On the contrary, in the absence of LM, a suppressed bimolecular termination between growing polymer radicals would be induced easily with conversion as a reflection of not only a well-known increased viscosity of the bulk polymerization system, but also a branching of the growing polymer radical generated by its intermolecular crosslinking reaction with the pendant double bond of the prepolymer [15,16]. The latter crosslinking reaction induces the increase of the number of primary chains in the prepolymer and thus, the extent of intramolecular crosslinking becomes higher; this would complicate the prepolymer structure leading to the enlargement of the primary chain length as a result of suppressed bimolecular termination, in which the living-type radical is formed, playing an important role for microgelation.

3.2. Variation of molecular weight distributions of resulting prepolymers with conversion

Fig. 2 shows the variation of SEC curves of the resulting prepolymers with conversion for the polymerization of NPGDMA as compared to DAT, in which NPGDMA was polymerized as described above and DAT was polymerized in bulk using 0.05 mol/l of BPO at 80°C. Clearly, quite similar curves were obtained for both the polymerizations of NPGDMA and DAT as typical examples for vinyl and allyl polymerizations, respectively. In addition, Fig. 2 indicates almost no occurrence of an intermolecular crosslinking reaction at the theoretical gel point conversion since the theoretical gel points are estimated to be 3.1 and 4.5% for NPGDMA and DAT polymerizations as is discussed later; even at conversions of 8.1 and 9.1%, more than twice that of the theoretical gel points, only a slight occurrence of intermolecular crosslinking was observed.

3.3. Deviation of actual gel points from theoretical ones

As the percentage of the gel polymer is shown in Fig. 1,

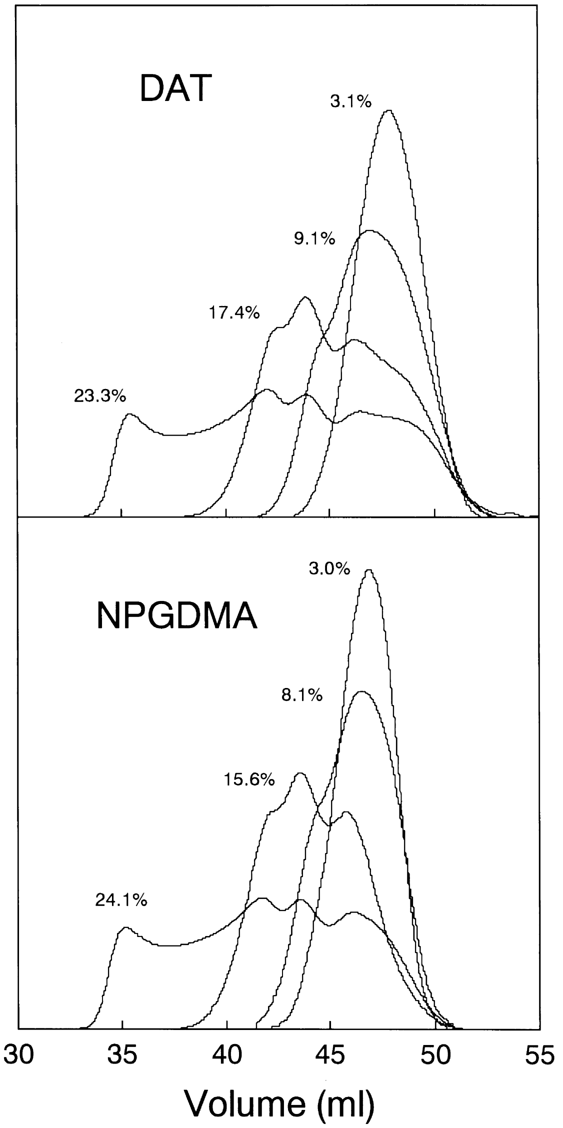

Fig. 2. Variation of SEC curves with conversion for the polymerizations of NPGDMA (see Fig. 1) and DAT (in bulk, [BPO] = 0.05 mol/l, 80°C).

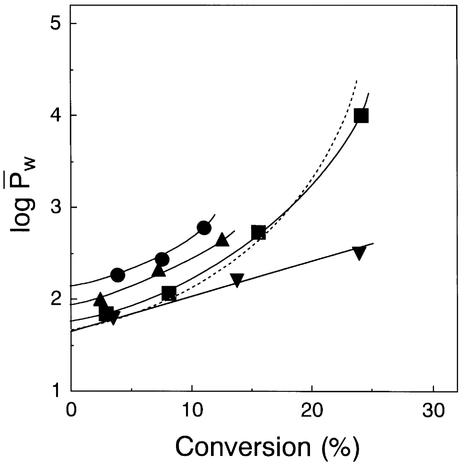

Fig. 3. Dependence of $\overline{P}_w$ on conversion in the polymerization of NPGDMA (see Fig. 1; [LM]/[NPGDMA] = (●) 1/20, (▲) 1/15, (■) 1/10, and (▼) 1/5) and DAT (see Fig. 2; dotted line).

the actual gel point was determined by extrapolating the gel formation curve to zero percentage; here the conversion at which gel starts to form, i.e. the gel point, was estimated to be 24.3%.

On the other hand, the theoretical gel point was calculated according to Gordon's equation [17]:

$$(1 - b_c) = 1 - [\{r(2\overline{P}_w - 3) - 1\}/\{r(2\overline{P}_w - 3) + 1\}]^2$$

where $(1 - b_c)$ is the conversion of the monomer at the gel point, r the fraction of monomer units having pendant double bond in the polymer, and $\overline{P}_w$ the weight-average number of divinyl monomer units per chain.

Now, we need to estimate the values of both r and $\overline{P}_w$. For the bulk polymerization of NPGDMA, the r value was assumed to be unity in reasonable agreement with the ^{1}H-NMR spectrum of the resulting poly(NPGDMA). The primary chain length $\overline{P}_w$ was estimated by the extrapolation of the conversion dependence of the weight-average degree of polymerization of the prepolymer determined by SEC-MALLS to zero conversion as shown in Fig. 3.

Table 1
Deviation of actual gel points from theoretical ones in the bulk polymerizations of NPGDMA ([ACHCN] = 0.01 mol/l, 50°C), HDMA ([ACHCN] = 0.01 mol/l, 50°C) and DAT ([BPO] = 0.1 mol/l, 80°C)

		$\overline{P}_{w,0}$	r[a]	Gel point (%)		Actual GP/theoretical GP
				Theoretical[b]	Actual[c]	
[LM]/[NPGDMA]	1/20	142	1	1.4	18	13
	1/15	92	1	2.2	21	9.6
	1/10	64	1	3.1	24.3	7.7
	1/5	47	1	4.3	34.5	8.0
[LM]/[HDMA]	1/10	64	0.9	3.5	24.7	7.2
	1/5	39	0.9	5.8	31.8	5.5
DAT		49	0.910	4.5	23.5	5.2

[a] Fraction of monomer units having pendant double bond in the primary chain.
[b] Theoretical gel point: $(1 - b_c) = 1 - (\{r(2\overline{P}_w - 3) - 1\}/\{r(2\overline{P}_w - 3) + 1\})^2$.
[c] Obtained as monomer basis.

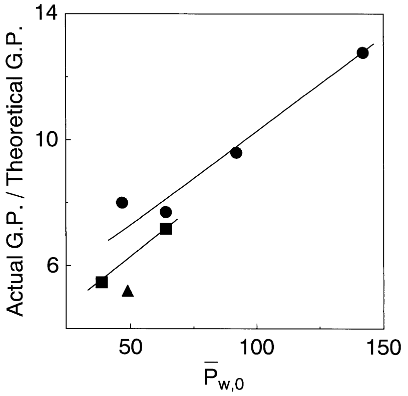

Fig. 4. Relationship between the ratio of actual gel point to the theoretical gel point and primary chain length for the polymerizations of (●) NPGDMA, (▲) DAT, and (■) HDMA.

Table 1 summarizes the results obtained for the polymerizations of NPGDMA under various conditions, along with the bulk polymerization result of DAT; the actual gel point was quite delayed from the theoretical one for each polymerization system. Fig. 4 shows the plots of the deviation of the actual gel point from the theoretical one against the primary chain length of the resulting prepolymer; the deviation became smaller with a decrease in the primary chain length. The comparison of NPGDMA with DAT revealed the rather greater delayed gelation for NPGDMA polymerization; this may be due to the rigidity of the primary chain. In order to clarify the correlation of the delayed gelation and the chain rigidity, HDMA was polymerized in bulk using 0.01 mol/l of ACHCN at 50°C in the presence of LM ([LM]/[HDMA] = 1/10 and 1/5); the results are shown in Table 1 and Fig. 4. The deviation of the actual gel point from the theoretical one became very close to DAT polymerization, probably as a reflection of flexible chain.

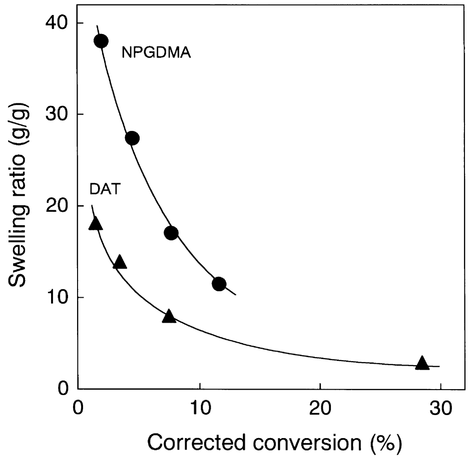

Fig. 5. Decrease in swelling ratio of resulting gel in benzene with the progress of polymerization beyond the gel point for the polymerization of NPGDMA in the presence of LM ([LM]/[NPGDMA] = 1/10), along with the bulk polymerization of DAT. Conversion in abscissa is corrected such that the corresponding gel point is zero percent of conversion.

3.4. High swelling ratio of the resulting gel obtained just beyond the gel point

The above results are in conformity with no occurrence of microgelation during the polymerization until the gel point conversion and, in addition, the polymerization solution was transparent, although it became turbid in the cases where microgelation occur [18].

Moreover, the variation of swelling ratios of resulting gels with the progress of polymerization beyond the gel point was examined for both NPGDMA and DAT polymerizations as shown in Fig. 5. Clearly, the swelling ratios of the gels obtained just beyond the gel points were very high for both polymerizations. This strongly suggests that no microgelation was observed up to the gel point in the polymerization of NPGDMA in the presence of LM as was the case for DAP polymerization [2].

4. Conclusion

In order to remove the obstacles in allyl and vinyl polymerizations for the discussion of network formation mechanism in the free-radical crosslinking polymerization of multivinyl compounds, the gelation behavior of NPGDMA in the presence of LM as chain transfer agent was explored in detail, the primary chain length being reduced down to a comparable order in allyl polymerization. Thus, no substantial difference was observed between allyl and vinyl polymerizations in the case where the primary chain lengths were adjusted to be comparable. In addition, no microgelation occurred up to the gel point.

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