

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



## Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

### Comparison of Gelation in the Free-Radical Polymerization of Triallyl Isocyanurate and its Isomer Triallyl Cyanurate

Akira Matsumoto<sup>a</sup>; Hiroyuki Inoue<sup>a</sup>; Tsukasa Matsumoto<sup>a</sup>; Masayoshi Iwa<sup>a</sup>; Tomiaki Kimura<sup>b</sup>; Hiroyasu Saito<sup>b</sup>

<sup>a</sup> Department of Applied Chemistry Faculty of Engineering, Kansai University, Suita, Osaka, Japan <sup>b</sup> Nippon Kasei Chemical Co., Ltd., Fukushima, Japan

**To cite this Article** Matsumoto, Akira , Inoue, Hiroyuki , Matsumoto, Tsukasa , Masayoshi Iwa, Kimura, Tomiaki and Saito, Hiroyasu(1989) 'Comparison of Gelation in the Free-Radical Polymerization of Triallyl Isocyanurate and its Isomer Triallyl Cyanurate', *Journal of Macromolecular Science, Part A*, 26: 9, 1279 – 1289

**To link to this Article:** DOI: 10.1080/00222338908052048

**URL:** <http://dx.doi.org/10.1080/00222338908052048>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

## COMPARISON OF GELATION IN THE FREE-RADICAL POLYMERIZATION OF TRIALLYL ISOCYANURATE AND ITS ISOMER TRIALLYL CYANURATE

AKIRA MATSUMOTO,\* HIROYUKI INOUE, TSUKASA MATSUMOTO,  
and MASAYOSHI OIWA

Department of Applied Chemistry  
Faculty of Engineering  
Kansai University  
Suita, Osaka 564, Japan

TOMIAKI KIMURA and HIROYASU SAITO

Nippon Kasei Chemical Co., Ltd.  
34 Takayama, Onahama, Iwaki-shi, Fukushima 971, Japan

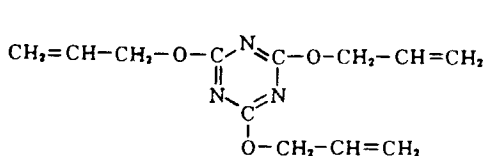
### ABSTRACT

Free-radical polymerizations of triallyl cyanurate (TAC) and its isomer triallyl isocyanurate (TAIC) were conducted in bulk at 60°C. In the polymerization of TAIC, gelation occurred at 12.4% conversion, quite early compared to 21.3% for TAC. The primary chain length of TAIC polymer, as estimated from GPC-LALLS measurements, was quite high. Although TAIC undergoes more cyclic polymerization than TAC, its greater primary chain length causes it to gel at a lower conversion. On the other hand, the difference in the rate of polymerization between TAC and TAIC was quite small compared to that of the primary chain length. These results are discussed mechanistically in connection with the degradative chain transfer characteristics of the polymerization of allyl compounds.

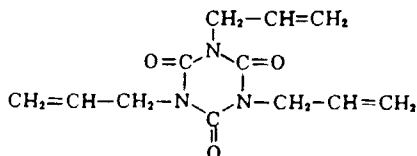
### INTRODUCTION

Triallyl cyanurate (TAC) and its isomer triallyl isocyanurate (TAIC) monomers are commercially important as crosslinking agents with comonomers and

for aftercuring preformed polymers, such as olefin copolymers, in electrical insulations [1]. They have also found use as crosslinking agents for unsaturated polyester resins [2]. However, only few basic studies of the polymerization of both monomers have been published [3, 4] although the monomer reactivity ratios with common vinyl monomers have been reported [5-7].



Triallyl cyanurate (TAC)



Triallyl isocyanurate (TAIC)

In our continuing studies of the free-radical polymerization of allyl compounds [8, 9], the polymerization behavior of TAC and TAIC were explored in detail. Interestingly, gelation occurred at quite a low conversion in the polymerization of TAIC compared to that of TAC. The primary chain length of TAIC polymer was quite high. The cyclopolymerizability of TAIC was greater than that of TAC. Thus, the unreacted pendent double bonds that are responsible for crosslinking of poly(TAIC) were less abundant than those of poly(TAC) as a reverse result of the promoted gelation. These results are discussed from a mechanistic standpoint.

## EXPERIMENTAL

TAC and TAIC monomers were supplied by Nippon Kasei Chemical Co. They were purified by vacuum distillation under nitrogen.

2,2'-Azobisisobutyronitrile (AIBN), the initiator, was purified by the conventional method.

Polymerization was carried out in ampules, as described previously [10]. After the desired time, the reaction mixture was poured into a large amount of hexane for TAC, or chilled methanol ( $-78^\circ\text{C}$ ) for TAIC, to precipitate the polymer. The purification of the polymer was done by reprecipitation from a benzene-precipitant system.

The gel fraction of polymer samples obtained at conversions beyond the gel point was isolated by extracting the sol fraction with benzene. The unreacted pendent allyl groups of the polymer were calculated from the iodine value obtained by the Wijs method.

GPC-LALLS measurements were carried out with a Waters Associate ALC/

GPC 244 apparatus at room temperature under the following conditions: solvent, tetrahydrofuran; TSK gel column combination, G2000H6, G3000H6, G4000H6, G5000H6, and G6000H6 (TOSOH designation); polymer concentration, 0.25% (w/v); and flow rate, 1 mL/min. The dual detector system consisted of a LALLS and a differential refractometer in sequence in the flow direction. The LALLS was a LS-8000 manufactured by TOSOH Corporation with a 6328 Å laser beam focused on a 30- $\mu$ L flow cell. The scattering angle was always 5°. The GPC curves monitored by differential refractometer were analyzed by using a calibration curve obtained with standard samples of mono-disperse polystyrene to estimate the molecular weight.

## RESULTS AND DISCUSSION

### Bulk Polymerization Results

Figure 1 shows the time-conversion curves for bulk polymerizations of TAC and TAIC along with the polymerization of diallyl phthalate (DAP) as a typical diallyl dicarboxylate for comparison. The overall rates of polymerization,  $R_p$ , of TAC and TAIC were estimated to be  $3.2 \times 10^{-5}$  and  $3.4 \times 10^{-5}$  mol/L·s, respectively, which are  $\sim 3$  times the value of  $1.0 \times 10^{-5}$  mol/L·s for DAP.

The percentage of gel polymer is also plotted in Fig. 1. The conversion at which gel starts to form, i.e., the gel point, was 21.3 and 12.4% for TAC and TAIC, respectively, compared to 23.5% for DAP polymerization. Interestingly, gelation occurred much earlier for TAIC. The amount of unreacted pendent allyl groups in the polymer, which are responsible for the crosslinking reaction, and the primary chain length will be discussed below.

No Trommsdorff effect [11] was observed, even beyond the gel point. This may be due to chain transfer from the growing polymer radical to the monomer (called degradative chain transfer [12]), which is very significant in the polymerization of allyl compounds, i.e., the allylic monomer radical plays an important role in the termination reaction.

### Cyclopolymerizability and Primary Chain Length

Figure 2 shows the residual unsaturation,  $R_{uS}$ , which would be 0.667 if no cyclization and crosslinking reactions occurred. The conversion dependence of  $R_{uS}$  may be attributed to the enhanced crosslinking and cyclization with conversion, the latter being caused by the decreased monomer concentration with conversion.

The initial residual unsaturation, obtained by extrapolation to zero conversion, was 0.643 and 0.567 for TAC and TAIC, respectively. In the early stages,

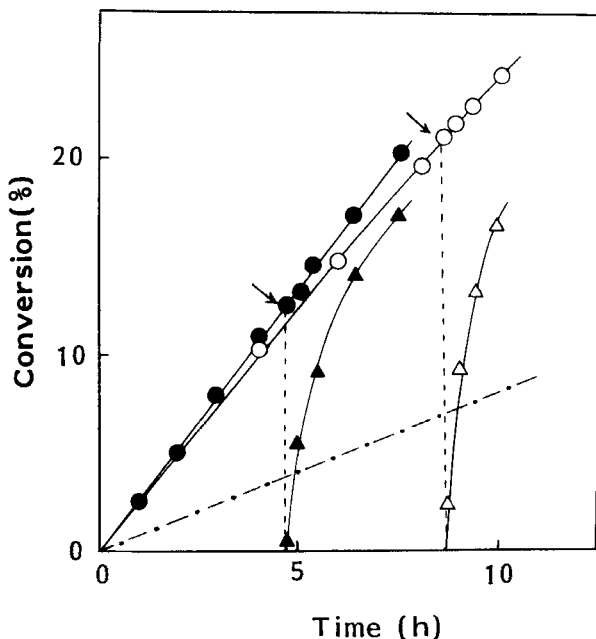


FIG. 1. Time-conversion curves for bulk polymerization of TAC and TAIC with 0.05 mol/L of AIBN at 60°C: (○ or ●) TAC or TAIC total polymer; (△ or ▲) TAC or TAIC gel polymer; (↓) gel point; (---) bulk polymerization result of diallyl phthalate for comparison.

crosslinking should be negligible, and therefore the deviation of the initial unsaturation from 0.667 may be ascribed predominantly to intramolecular cyclization. Thus, the cyclopolymerizability of TAIC is higher than that of TAC.

The ratio of the rate constant for the unimolecular cyclization reaction to that for the bimolecular propagation of the uncyclized radical,  $K_c$ , was evaluated to be 0.53 and 3.0 mol/L for TAC and TAIC, respectively, by using the kinetic equation derived for the cyclopolymerization of triallyl citrate [13]. The number of unreacted allyl groups per structural unit in the initial polymer or primary chain, is calculated to be 1.93 and 1.70 for TAC and TAIC, respectively. This shows that the primary chains of both TAC and TAIC polymers contain enough pendent allyl groups for crosslinking and, thus, the difference in the cyclopolymerizability between TAC and TAIC is not the reason for the enhanced gelation in TAIC polymerization.

The TAIC GPC curves (Fig. 3) were broadened toward lower elution volume

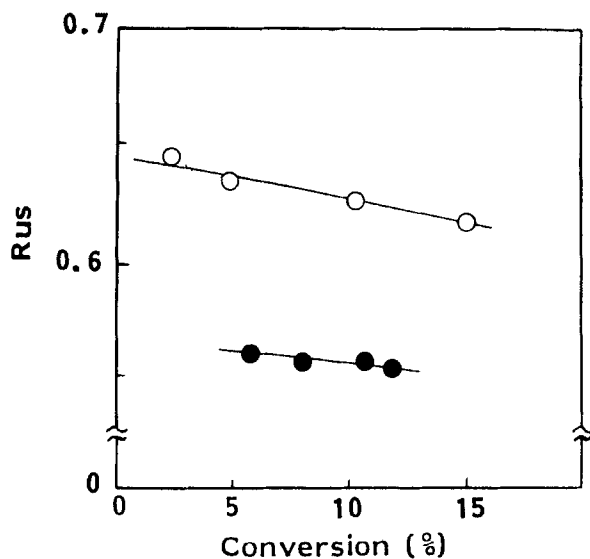


FIG. 2. Dependence of the residual unsaturation,  $R_{us}$ , on conversion for bulk polymerization of (○) TAC and (●) TAIC at 60°C.  $R_{us}$  is expressed as the fraction of the unsaturation in pure monomer.

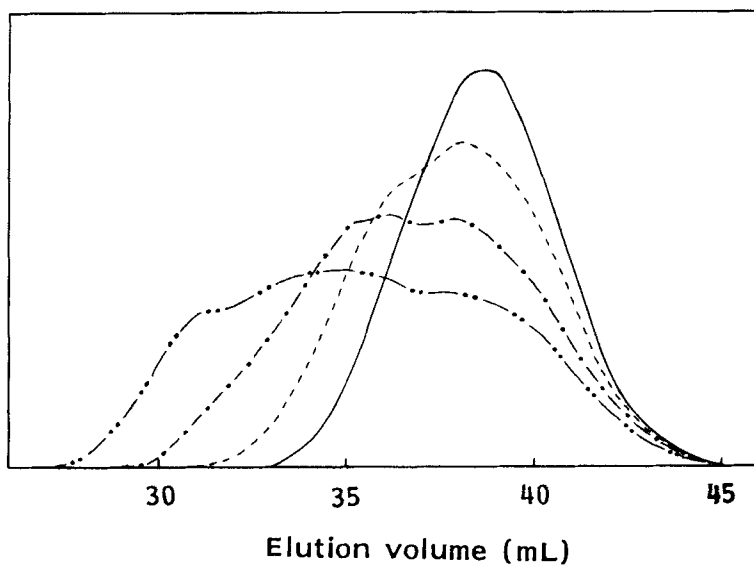


FIG. 3. Variation of GPC curves with conversion for bulk polymerization of TAIC at 60°C. Conversion: (—) 2.4%, (---) 4.7%, (-·-) 7.1%, and (-·-·) 9.8%.

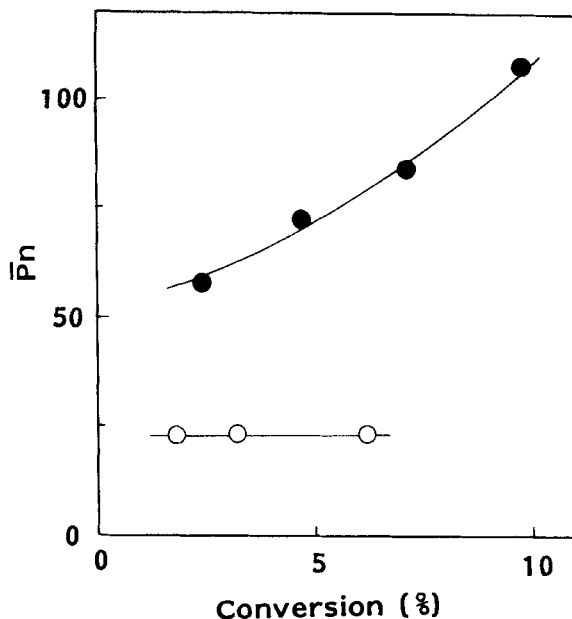


FIG. 4. Dependence of the number-average  $DP$ ,  $\bar{P}_n$ , on conversion for bulk polymerization of (○) TAC and (●) TAIC at 60°C.  $\bar{P}_n$  obtained from GPC with a refractive index monitor.

at high conversions, which reflects the occurrence of intermolecular crosslinking. The GPC curves were analyzed to estimate  $\bar{M}_n$  and  $\bar{M}_w$ . Figure 4 shows the dependence of the number average degree of polymerization,  $\bar{P}_n$ , on conversion. Interestingly, the  $\bar{P}_{n,0}$  value, extrapolated to zero conversion, of the TAIC polymer, i.e., the "primary chain length," was quite high at  $\sim 53$ , and 2.3 times greater than that of TAC. However, the polydispersity  $\bar{P}_w/\bar{P}_n$  (Fig. 5) extrapolates to  $\sim 2$  at zero conversion. In this connection,  $\bar{P}_{n,0}$  was 32 for DAP [14], and generally,  $\bar{P}_n$  would be much lower for the polymerization of allyl compounds. This high  $\bar{P}_{n,0}$  value for TAIC polymerization was estimated from the analysis of GPC curves monitored by differential refractometry. The relationship between the molecular weight and size for the TAIC polymer may be quite different from that for the polystyrene standard, although the difference between TAC and TAIC polymers should be quite small. Therefore, we tried to determine the weight-average molecular weight by light scattering.

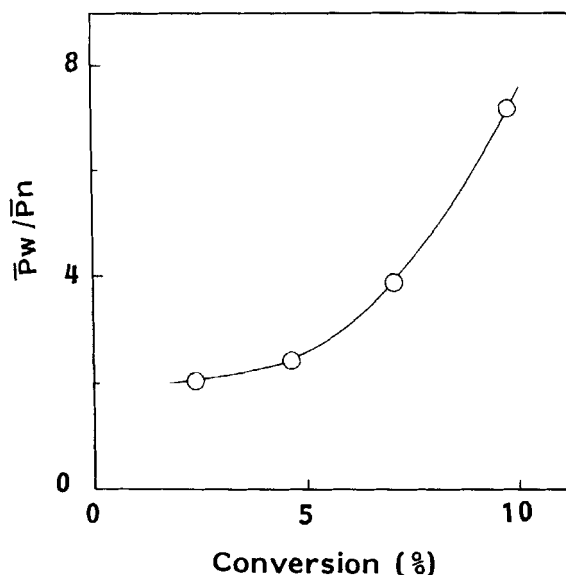


FIG. 5. Dependence of the polydispersity  $\bar{P}_w/\bar{P}_n$  on conversion for bulk polymerization of TAIC at 60°C.

Figure 6 shows both GPC curves of the TAIC polymer obtained at 4.7% conversion as an example. Comparison of the two curves shows that the light scattering is greater in the high-molecular-weight range, suggesting that the high molecular-weight molecules are smaller in solution, probably due to intramolecular crosslinking.

The RI- and the LALLS-monitored curves were analyzed to estimate  $\bar{P}_w$ , and the ratio is shown in Fig. 7. The ratio increased from 3.2 at 2.4% conversion to 6.1 at 9.8%. This increase with conversion may be indicative of increased intramolecular crosslinking and a concomitant decrease of the molecular size in solution. Moreover, the  $\bar{P}_{w,0}$  (LALLS) value for the primary chain of TAIC polymer, as estimated from the data in Fig. 6 by extrapolating to zero conversion, was  $\sim 3$  times higher than  $\bar{P}_{w,0}$  (RI), probably owing to a large  $Q$ -factor or bulky substituents and the formation of large rings through nonconsecutive intramolecular addition, as has been observed for the polymerization of diallyl terephthalate [15-17].

In conclusion, the primary chain length of TAIC polymer is quite high,  $\bar{P}_{n,0} \approx 160$ , and this is a main reason for the enhanced gelation since TAIC is



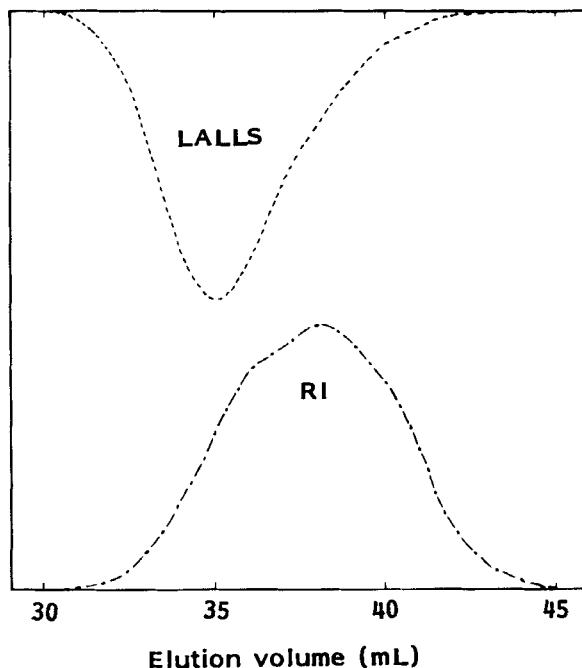


FIG. 6. GPC curves with LALLS and refractive index monitors for TAIC polymer obtained at 4.7% conversion.

a typical allyl compound. However, the rates of polymerization of both TAC and TAIC were almost equivalent.

### Mechanistic Discussion

As mentioned above, the primary chain length of TAIC polymer was quite high. Recall that in free-radical polymerization of allyl compounds, degradative chain transfer [12], i.e., chain transfer of the growing polymer radical to monomer, is very important and is an essential termination reaction. Thus the monomer chain transfer constant,  $C_m (= k_{tr,m}/k_p)$ , i.e., the ratio of the rate constant of monomer chain transfer to that of propagation of the growing polymer radical, will determine the degree of polymerization. The  $k_p$  values are not expected to be different for TAC and TAIC because the reactivity ratios of both monomers toward methyl methacrylate, styrene, and

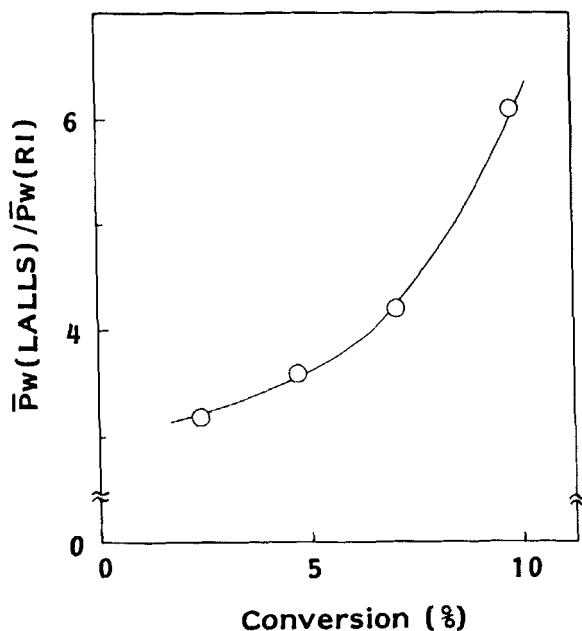
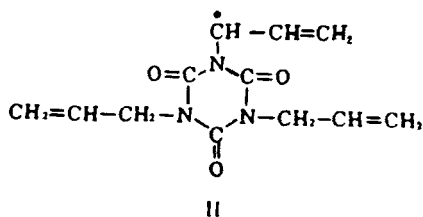
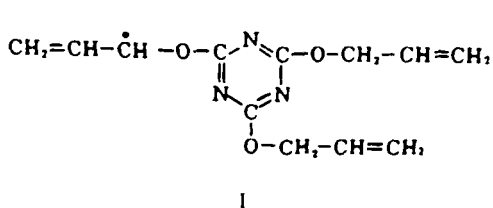


FIG. 7. Dependence of the  $\bar{P}_w(\text{LALLS})/\bar{P}_w(\text{RI})$  ratio on conversion for bulk polymerization of TAIC at 60°C.

vinyl acetate are essentially equivalent [5], while  $k_{tr,m}$  for TAIC should be smaller than that for TAC. This effect may be due to steric hindrance, as expected from the following structures of the TAC (I) and TAIC (II) allyl radicals:



which show that an oxygen atom intervenes between the allyl radical and the cyanuric ring in I, but not in II. This will induce steric hindrance for monomer chain transfer although propagation occurs by attack of the growing polymer radical toward the  $\gamma$ -site of the vinyl methylene carbon.

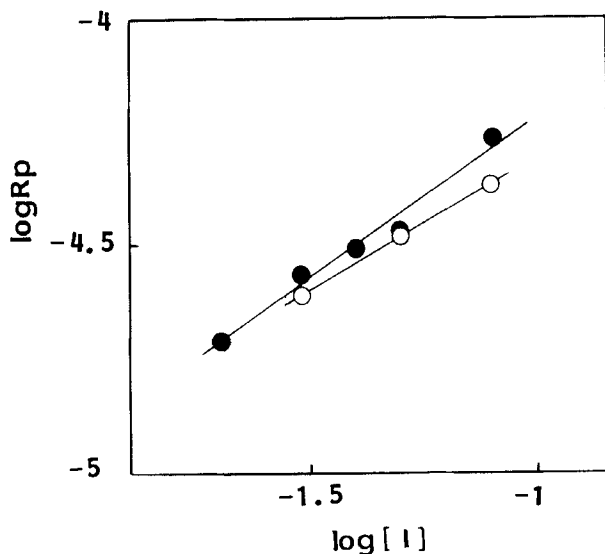


FIG. 8. Double logarithmic plots of polymerization rate  $R_p$  vs initiator concentration  $[I]$  for bulk polymerization of (○) TAC and (●) TAIC at  $60^\circ\text{C}$ .

This reduced occurrence of monomer chain transfer may also explain the slightly enhanced polymerization rate when the probabilities of the resulting allyl radicals, I and II, to reinitiate are the same. In order to reconcile the latter with the almost equal  $R_p$  values, we propose a reduced reinitiation ability of the TAIC allyl radical compared to the TAC allyl radical because the electron density of the former will be lowered by the strong electron-withdrawing nature of the isocyanuric ring. Hence, the dependence of  $R_p$  on initiator concentration was then examined.

The reaction orders with respect to initiator concentration were estimated to be 0.56 and 0.70 for TAC and TAIC, respectively, from the logarithmic plots in Fig. 8. The higher order in TAIC suggests the importance of degradative chain transfer [12], as expected.

#### ACKNOWLEDGMENTS

The authors are grateful to Messrs. Tsukasa Matsumoto and Hiroyuki Inoue for their helpful assistance.

## REFERENCES

- [1] C. E. Schildknecht, in *Encyclopedia of Polymer Science and Engineering*, Vol. 4, 2nd ed., Wiley-Interscience, New York, 1986, p. 779.
- [2] E. J. Sare, in *Modern Plastics Encyclopedia (1986-1987)*, Vol. 63, No. 10A, McGraw-Hill, New York, 1987, p. 16.
- [3] M. Oiwa and W. Kawai, *Nippon Kagaku Zhasshi*, 76, 107 (1955).
- [4] B. H. Clampitt, D. E. German, and J. R. Galli, *J. Polym. Sci.*, 27, 515 (1958).
- [5] R. W. Roth and R. F. Church, *Ibid.*, 55, 41 (1961).
- [6] M. Kucharski and A. Rytzel, *J. Polym. Sci., Polym. Chem. Ed.*, 16, 3011 (1978).
- [7] M. Kucharski and A. Rytzel, *Polymer*, 25, 555 (1984).
- [8] M. Oiwa and A. Matsumoto, in *Progress in Polymer Science Japan*, Vol. 7, Kodansha, Tokyo, 1974, p. 107.
- [9] A. Matsumoto, *Netsukokasei Jushi (J. Thermoset. Plast., Jpn.)*, 8, 99 (1987).
- [10] A. Matsumoto and M. Oiwa, *J. Polym. Sci., Part A-1*, 8, 751 (1970).
- [11] E. Trommsdorff, H. Kohle, and P. Lagally, *Makromol. Chem.*, 1, 169 (1948).
- [12] P. D. Bartlett and R. Altschul, *J. Am. Chem. Soc.*, 67, 812, 816 (1945).
- [13] A. Matsumoto, T. Ohata, and M. Oiwa, *Bull. Chem. Soc. Jpn.*, 47, 673 (1974).
- [14] A. Matsumoto, S. Yokoyama, T. Khono, and M. Oiwa, *J. Polym. Sci., Polym. Phys. Ed.*, 15, 127 (1977).
- [15] T. Holt and W. Simpson, *Proc. R. Soc., London*, A238, 154 (1956).
- [16] A. Matsumoto and M. Oiwa, *Nippon Kagaku Zasshi*, 90, 1278 (1969).
- [17] A. Matsumoto, H. Sasaki, and M. Oiwa, *Makromol. Chem.*, 166, 179 (1973).

Received June 24, 1988

Revision received August 15, 1988