Macromol. Symp. 132, 431-440 (1998)

SPECIFIC PHENOMENA DURING THE COPOLYMERIZATION OF TRIOXANE AND ETHYLENE OXIDE

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Abstract: We, at Asahi Chemical in Japan, have industrialized three types of polyacetal resins, that is, the acetal homopolymer, copolymer and block copolymer using anionic, cationic and anionic polymerization techniques, respectively. During this industrialization, we observed various phenomena, which were not previously reported. First, the authors outline the three technologies for producing each type of polyoxymethylene from an industrial viewpoint. Next, the authors discuss a newly found reaction during the induction period of the trioxane and ethylene oxide copolymerization. Experimental proof of direct ring expansion between the reaction of trioxane and ethylene oxide is discussed and various novel cyclic compounds are also shown. To the best of our knowledge, this reaction may be the world's first experimental proof of direct ring expansion of the reaction of a cyclic monomer. Third, the authors also discuss the newly founded morphospecific polymer from the copolymerization of trioxane and ethylene oxide using boron trifluoride dibutyl ether as an initiator.

INTRODUCTION

Polyoxymethylene is one of the most useful engineering plastics, which is produced from the polymerization of formaldehyde or the copolymerization of trioxane with cyclic ether using ionic polymerization techniques. We, at Asahi Chemical in Japan, industrialized three types of polyacetal resins --- the acetal homopolymer, acetal copolymer and acetal block copolymer, using anionic, cationic, and anionic polymerization techniques, respectively. During this industrialization, we observed various new phenomena, which have not been previously reported.

This paper consists of three parts. The first part is an outline of Asahi Chemical's polyacetal technologies, which were developed and industrialized by the authors. The second part is concerned with the newly found reaction between trioxane and ethylene oxide during the induction period of trioxane and ethylene oxide copolymerization. In this part we discussed the nature of this ring expansion reaction and its mechanism. The third part is about a morphospecific polymer obtained from the copolymerization of trioxane and

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CCC 1022-1360/98/$ 17.50

ethylene oxide using boron trifluoride dibutyl ether as an initiator. This morphospecific phenomena are characteristic phenomena only found in trioxane copolymerization manufacturing process and not observed in the formaldehyde polymerization acetal homopolymer process.

1. Outline of Asahi Chemical's Three Polyacetal Resins Manufacturing Technologies Using Ionic Polymerization Techniques

We have industrialized three types of polyacetal resins, that is, the acetal homopolymer, copolymer and block copolymer using anionic, cationic and anionic polymerization techniques, respectively (Ref. 1).

As the raw material for polyoxymethylene, formalin is used. Formalin is usually obtained by the methanol oxidation technique. In this case, from 50 to 55 wt.-% formalin is obtained. However the author developed a new formaldehyde manufacturing technology, that is, the methylal oxidation technology (Ref. 1). In this methylal oxidation process, highly concentrated formalin, about 70 wt.- %, can be obtained. The manufacture of this highly concentrated aqueous formaldehyde solution give us process innovation for manufacturing polyacetal resins.

1.1 Acetal Homopolymer

Conventionally, formaldehyde is purified prior to the polymerization, however, it contains a certain amount of impurities such as water, methanol, formic acid, etc.

Thus, when the formaldehyde is polymerized to polyoxymethylene and when water acts as a chain transfer agent, the polymer ends were the thermally unstable -OH group. Thus, the thermally unstable polymer end group of -OH is end-capped by acetylation with acetic anhydride (Ref. 1). In this case, several parts of the polymer are lost due to the unzipping from the unstable polymer end groups.

We developed a new process for manufacturing the acetal homopolymer. The highly purified formaldehyde is polymerized using an anionic polymerization initiator, such as a quaternary ammonium salt, in the presence of acetic anhydride as the chain transfer agent or end-capping agent. Thus end-capping simultaneously occurred during the polymerization (Ref. 1). An example of the excellent purification technology of formaldehyde has been invented by the authors (Ref. 2).

1.2 Acetal Copolymer

Conventionally, polymerization grade trioxane contains some impurities, such as water, methanol, formic acid, etc. When the trioxane is copolymerized with a cyclic ether such as ethylene oxide or 1,3-dioxolane, the polymer end groups are thermally unstable$(CH_2O)_n$-OH groups. Thus the thermally unstable polymer end is unzipped to the thermally stable $-CH_2CH_2$-OH groups (Ref. 1).

We have developed a new process for manufacturing the acetal copolymer. Highly purified trioxane is copolymerized with ethylene oxide using a cationic polymerization initiator, such as boron trifluoride dibutyl ether, in the presence of methylal as a chain transfer agent or an end-capping agent. Thus end-capping simultaneously occurred during the polymerization (Ref. 1). An example of the excellent purification technology of trioxane has also been developed by the author (Ref. 3).

1.3 Acetal Block Copolymer

The acetal block copolymer is obtained by the polymerization of formaldehyde in the presence of the functional polymer, RO(X)mH, which has an active hydrogen atom (eq. 1) (Ref. 4).

$$nCH_2O + RO(X)_mH \rightarrow RO(X)_m(CH_2O)_nH \qquad (1)$$

In this case, RO(X)mH is the lubricant functional polymer.

This functional polymer block, RO(X)m, is chemically bonded with the polyoxymethylene block. This acetal block copolymer shows superior lubrication properties compared to ordinary lubricant-blended polyoxymethylene.

1.4 Nylon 3 as a New Stabilizer for Polyoxymethylene

For high quality products, we developed a special stabilizer for polyoxymethylene. Conventionally, nylon 6-66-610 is used for the stabilizer as the formaldehyde scavenger. We developed nylon 3 as the polyoxymethylene stabilizer.

Nylon 3 was first synthesized by Breslow et al. by the hydrogen transfer polymerization of acryl amide (Ref. 5). Next, Masamoto et al. at Asahi Chemical made nylon 3 fiber and clarified properties and structure of nylon 3 first in the world (Refs. 6, 7). Finally, researchers at Asahi Chemical found that nylon 3 is a excellent stabilizer for polyoxymethylene (Ref. 8).

Futures of nylon 3 as the stabilizer for polyoxymethylene are as follows: high thermal stability, negligible discoloration when the molten polyoxymethylene remains injection mold machine for a long time, and low mold deposition for a long time use.

2. New Reaction between Trioxane and Ethylene Oxide and Novel Cyclic Compounds

We discovered a new reaction between trioxane and ethylene oxide.

The previously held theory concerning the mechanism of the copolymerization of trioxane and ethylene oxide, based on many experimental data, is that trioxane is first decomposed to form formaldehyde, and the formaldehyde then reacts with ethylene oxide to produce 1,3-dioxolane and 1,3,5-trioxepane (Refs. 9, 10). Weissermel et al. proposed this initiation mechanism (Ref. 9) and Collins et al. confirmed this mechanism and gave a more detailed discussion (Ref. 10). Previous work only shows the results of the reaction in the last stable zone.

The initiation mechanism during the bulk copolymerization of trioxane and ethylene oxide using boron trifluoride dibutyl ether as the initiator was carefully studied, and the new intermediates or novel cyclic compounds, 1,3,5,7-tetraoxacyclononane(TOCN) and 1,3,5,7,10-pentaoxacyclododecane (POCD), which disclosed the precise initiation mechanism as shown in Fig. 1, were isolated.

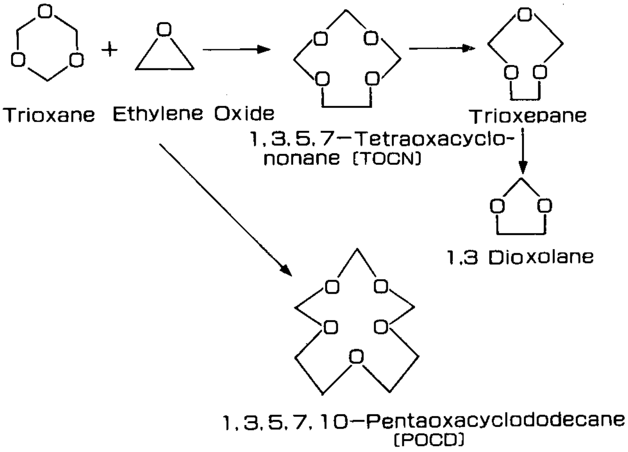

Fig. 1 Newly found copolymerization mechanism of trioxane and ethylene oxide

The Proton NMR charts of 1,3,5,7-tetraoxacyclononane(TOCN) and 1,3,5,7,10-pentaoxacyclododecane(POCD) are shown in Figures 2 and 3, respectively.

At first, ethylene oxide reacts with trioxane to produce TOCN or 1,3,5,7-tetraoxacyclononane which is the reaction product of 1 mole ethylene oxide and 1 mole trioxane, and POCD or 1,3,5,7,10-pentaoxacyclododecane, which is the reaction product of 2 moles ethylene oxide and 1 mole trioxane. From the former compounds, 1,3,5-trioxepane and 1,3-dioxolane result and are then copolymerized with trioxane.

This discovery has three important ramifications:

(1) It realizes a new reaction and various novel cyclic compounds, such as cyclic formal and a new type of crown ether.
(2) Industrially, it gives information about the trioxane-ethylene oxide copolymer reactor design.
(3) This reaction is an experimental proof of a cationically initiated direct ring expansion between the reaction of cyclic monomers.

As for the first item of this discussion, using gas chromatography we observed the various compounds, which are thought to be novel cyclic compounds. We checked the minor components of various reactants using the 10 mol- % ethylene oxide to trioxane mixture.

For example, presence of one of the novel cyclic compounds, 1,3,5,7,10,13-hexaoxacyclopentadecane (HOCP), which is thought to be the cyclic compounds of 3 moles of ethylene oxide and 1 mole of trioxane, is supposed to be formed, though this compound has not yet been isolated and its structure is not yet identified. One more new reaction is also postulated for the formation of 1,3,5,8-tetraoxacyclodecane from 1,3,5,7,10-pentaoxacyclododecane by the removal of formaldehyde, though 1,3,5,8-tetraoxacyclodecane, as the reaction product, is not identified. These

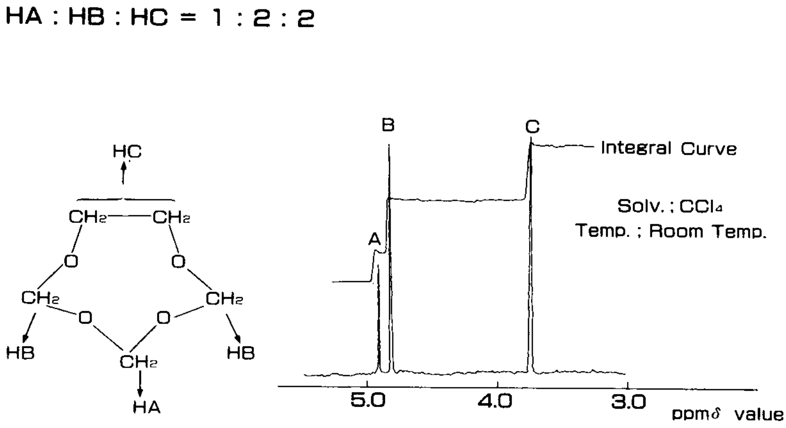

Fig. 2 Proton NMR pattern of 1,3,5,7-tetraoxacyclononane (TOCN)

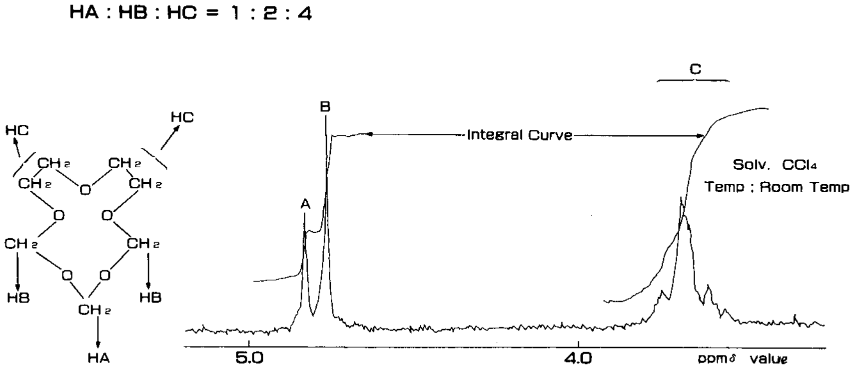

Fig. 3 Proton NMR pattern of 1,3,5,7,10-pentaoxacyclododecane (POCD)

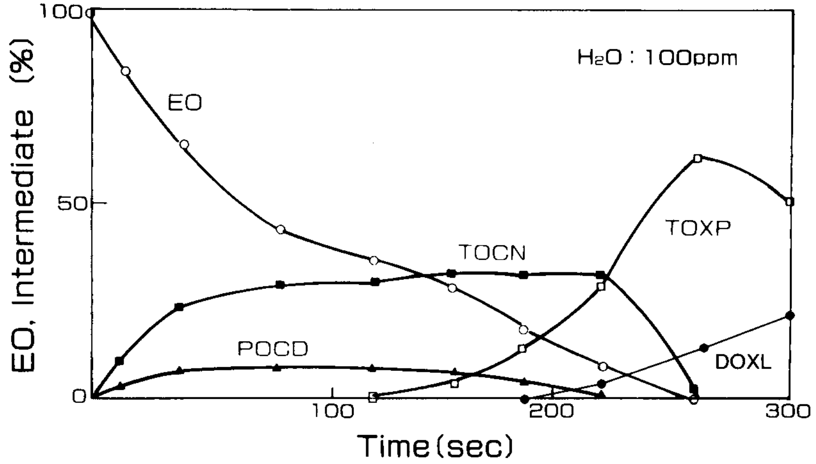

Fig. 4 Profile of reactants and intermediates in trioxane/ethylene oxide (4.5 mol-% trioxane) copolymerization (H_2O: 100 ppm)
EO: ethylene oxide, TOCN: 1,3,5,7-tetraoxacyclononane,
POCD: 1,3,5,7,10-pentaoxacyclododecane, TOXP: 1,3,5-trioxepane,
DOXL: 1,3-dioxolane

reactions will be confirmed in the near future.

Furthermore, we will also try to elucidate whether this reaction can be generalized for the reaction among cyclic formals and alkylene oxide, not being limited to the reaction between trioxane and ethylene oxide.

As for the second item of this discussion, from the discovery of this new reaction, we designed a trioxane-ethylene oxide polymerization reactor, which is very compact and effective for producing a high quality acetal copolymer product. We industrialized our first commercial trioxane ethylene oxide copolymer plant in Japan using this technique and the second commercial plant is scheduled to be operated in Singapore in late 1998.

As for the third item of this discussion, the conventionally reported mechanism of ring expansion is a back-biting mechanism of the linear active polymer chain end, as in the case of ring opening polymerization of tetrahydrofuran or 1,3-dioxolane (Ref. 11, 12). Formerly, Plesch originally proposed the direct ring expansion mechanism for the protonic acid-initiated polymerization of 1,3-dioxolane (Ref. 13), however, at present, these cyclic oligomers are thought to come from the back-biting mechanism (Ref. 11, 12).

However, in our case, considering the fact that 1,3,5,7-tetracyclononane, which is the reaction product of one mole of trioxane and one mole of ethylene oxide, is first formed and then 1,3,5-trioxepane appeared later and then a little later 1,3-dioxolane is formed. Experimental results showed that the reaction equilibrium between 1,3,5-trioxepane and 1,3-dioxolane exists, however, no equilibrium concentration of 1,3,5,7-tetraoxacyclononane exists.

Considering the fact that ring strain energy of a 9-ring cycloalkane is 27 kJ/mol higher than 7 and 5-ring cyclic alkanes (8), ring strain energy of 9-ring 1,3,5,7-tetraoxacyclononane is much higher than that of 7-ring 1,3,5-trioxepane and 5-ring 1,3-dioxolane. Thus, the equilibrium concentration of 1,3,5,7-tetraoxacyclononane is thought not to exist.

If the back-biting reaction is the source of larger sized cyclic compounds, only 1,3,5-trioxepane and 1,3-dioxolane should be formed and 1,3,5,7-tetraoxacyclononane should not be formed. However, 1,3,5,7-tetraoxacyclononane is experimentally formed first. From experimental observation of the behavior of 1,3,5,7-tetraoxacyclononane and the thermodynamic consideration made above, it is plausible to think that 1,3,5,7-tetraoxacyclononane is formed by the direct ring expansion reaction between 1,3,5-trioxane and ethylene oxide. As far as we know, our discovery of the formation of 1,3,5,7-tetraoxacyclononane from 1,3,5-trioxane and ethylene oxide is the wold's first experimental proof of direct ring expansion. However, further, a precise experimental proof is necessary to confirm our proposal.

3. Morphospecific Polymer from the Copolymerization of Trioxane and Ethylene Oxide

The copolymer from the copolymerization of trioxane and ethylene oxide is a useful engineering plastic which is called the acetal copolymer. Usually, the content of ethylene oxide is about 2 wt%. Its melting point is about 165 ° C, which is below that of the acetal homopolymer which is the product of formaldehyde using an anionic initiator such as the quaternary ammonium salt.

Recently, we found that there sometimes exists some fraction of the copolymer which has a higher melting point than that of the other fractions. We checked the nature of this high melting fraction.

The polymer as a powder was dissolved in the p-chlorophenol - tetrachloroethane mixed solvent at 90 ° C. In almost all of the polymerization cases, all polymers were soluble at this temperature. However, in some polymerization cases, a very small portion of the polymer was not soluble at this temperature.

The first scan of the DSC (differential scanning calorimeter) curves of the three types of polymers (sample 1: all soluble bulk polymer, sample 2: bulk polymer which contains a very small insoluble portion, sample 3: mixed solvent-insoluble polymer) were checked. Both bulk polymers (samples 1 and 2) showed a melting temperature of 165 ° C, while the mixed solvent-insoluble fraction (sample 3) showed a melting point over 170 ° C.

The second scan of the DSC curves of the three types polymers showed almost the same pattern. The chemical composition (comonomer content, comonomer sequences) and reduced viscosity of the three types of polymers were checked, and we found that there were no differences among them.

SEM (scanning electron microscope) photographs of the three types polymers were also checked. SEM photographs are shown in Fig. 5.

For sample 1, which contains no insoluble fraction, the fibril structure was very weak. For sample 2, which contains a small portion of the insoluble fraction, a fibril structure was observed. A highly fibril form was observed for the mixed solvent-insoluble fraction (sample 3), which suggests a dense

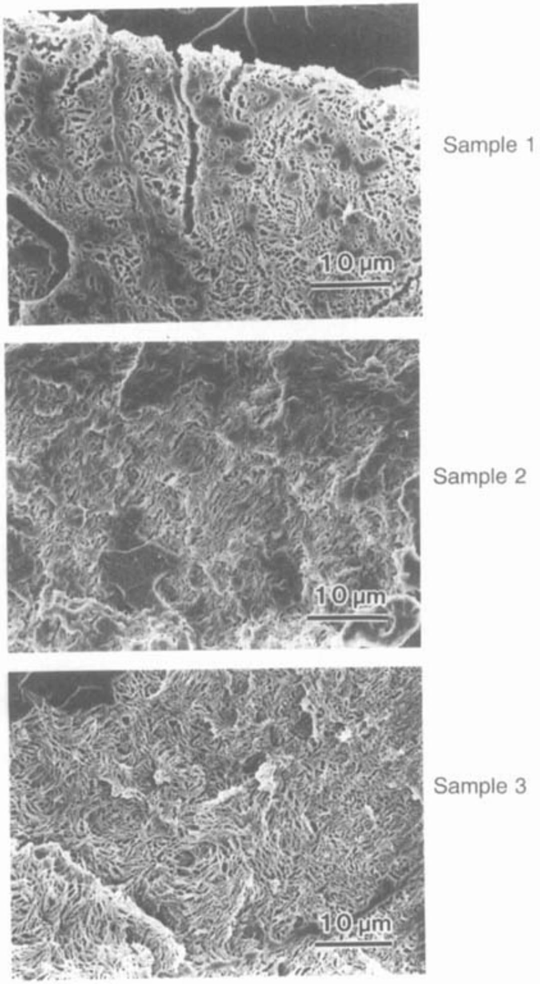

Fig. 5 SEM photographs of the three types polymers

packed crystalline structure. This highly packed structure is thought to be the origin of the high melting point.

The melt quenched spherulite of sample 3 gave a clear and strongly grown lammelae which formed spherulites bigger than those of sample 1 as shown in Fig. 6.

The highly fibril forms of sample 3 suggest a less entangled polymer chain, which lead to less nucleation of the spherulite and thus produced the strongly grown lammelae of spherulite.

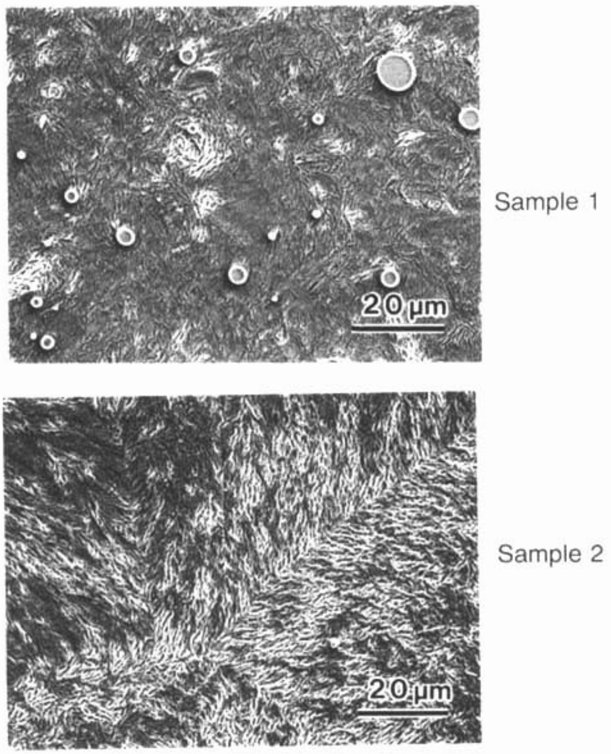

Fig. 6 SEM photographs of melt quenched spherulites of sample 1 and sample 3
Each samples was melted at 200 °C and quenched in water at room temperature

To check whether this morphospecific phenomenon is a characteristic phenomenon for trioxane polymerization products, we checked various acetal homopolymers, whose molecular weights are from 20,000 to 70,000 and which are anionically polymerized. We could not find any morphospecific phenomena for the acetal homopolymer. Thus, at present, to the best of our knowledge, we consider that the morphospecific phenomenon is a characteristic phenomenon for trioxane polymerization. This might be caused by the difference in crystallization during the polymerization between formaldehyde anionic polymerization and trioxane cationic polymerization. However, elucidation of the nature of this behavior is thought to be very complicated.

CONCLUSION

1. The development and industrialization of three types of polyoxymethylene was outlined, and two new previously unknown phenomena were found in the development of trioxane ethylene oxide copolymer.
2. The new reaction between trioxane and ethylene oxide gave the precise initiation reaction of trioxane and ethylene oxide copolymerization. This reaction also gives various novel cyclic compounds, and this reaction is thought to be experimental proof of the direct ring expansion between cyclic monomers.
3. Copolymerization of trioxane and ethylene oxide using boron trifluoride dibutyl etherate as an initiator gave a morphospecific polymer.

REFERENCES

(1) J. Masamoto, *Prog. Polym. Sci.* **18**, 1 (1993)
(2) *US Pat.* 4,962,235 assigned to Asahi Chemical
(3) *US Pat.* 4,493,752 assigned to Asahi Chemical
(4) *US Pat.* 4,377,667 assigned to Asahi Chemical
(5) D. S. Breslow, G. E. Hulse and S. Matlack, *J. Am. Chem. Soc.* **79**, 3760 (1957)
(6) J. Masamoto, K. Sasaguri, C. Ohizumi, K. Yamaguchi and H. Kobayashi, *J. Appl. Polym. Sci.* **14**, 667 (1970)
(7) J. Masamoto, K. Sasaguri, C. Ohizumi and H. Kobayashi, *J. Polym. Sci.*, Part A-2, **8**, 1703 (1970)
(8) *US Pat.* 4,855,365 assigned to Asahi Chemical
(9) K. Weissermel, E. Fisher, K. Guweiler, H. D. Hermann and H. Cherdron, *Angew. Chem. Int. Ed.* **6**, 526 (1967)
(10) G. L. Collins, R. K. Greene, F. M. Beradinelle and W. H. Ray, *J. Polym. Sci., Polym. Chem. Ed.* **19**, 1597 (1981)
(11) S. Penczek and S. Slomkowski, '*Cationic Ring-opening Polymerization: Formation of Cyclic Oligomers*', in '*Comprehensive Polymer Science*' ed. S. G. Allen, Pergoman Press, 1989, Vol 3, p. 725
(12) P. Kubisa, '*Cationic Polymerization of Heterocyclics*', in '*Cationic Polymerizations: Mechanism, Synthesis, and Applications*' ed. by K. Matyjaszewski, Dekker, 1995, p. 437
(13) P. H. Plesch and P. H. Westermann, *J. Polym. Sci.* C**16**, 3837 (1968)