PII: S0032-3861(97)10158-6

Polymer Vol. 39 No. 15, pp. 3583–3586, 1998

0032-3861/98/$19.00+0.00

Oligomerization mechanism of cyclohexene oxide

Shaobing Wu and Mark D. Soucek*
Department of Polymers and Coatings, North Dakota State University, Fargo, ND 58105, USA
(Received 20 May 1997; revised 18 September 1997; accepted 24 September 1997)

Oligomerization of cyclohexene oxide was studied in the presence of two competitive nucleophiles (methanol and acetic acid). The resulting oligomers, 2-methoxyl-2′-hydroxyl-dicyclohexyl ether (**II**) and 2-acetoxyl-2′-hydroxyl-dicyclohexyl ether (**IV**), were isolated and spectroscopically characterized. The formulation of these oligomers were evaluated as a function of the reactant molar ration, pH, and temperature. The reaction rate constants, and Arrhenius parameters for the formation of the oligomers were determined over a pH range of 4 to 7. The reaction rates for the formation of the oligomers exhibited a second order dependence on the concentration of cyclohexene oxide, and first order dependence on the nucleophile and proton concentration, respectively. The major reaction pathway proposed for the formation of the cyclohexene oxide oligomers was via an activated chain end complex. The propagation of the activated chain end complex was then terminated by nucleophile attack (methanol or acetic acid).

(Keywords: cyclohexene oxide; oligomerization; cycloaliphatic epoxides)

Introduction

Cycloaliphatic epoxides and phenyl glycidyl ethers are the two major types of epoxy resins utilized in the coatings industry. Cycloaliphatic epoxides are characterized by inherently low levels of ionic impurities, low resin viscosity, and high reactivity especially under cationically catalysed conditions[1]. Upon crosslinking, cycloaliphatic epoxides display several advantages over the phenyl glycidyl ethers. These advantages are excellent chemical resistance, photostability, and electrical and mechanical properties[2]. Because of these characteristics, cycloaliphatic epoxides have been extensively used as binders for cationic ultraviolet (u.v.) light cured overprint varnishes, inks, non-metal substrate (wood, paper, and plastic) coatings, and electrical/electronic coatings. Typically, difunctional cycloaliphatic epoxides such as 3,4-epoxycyclohexyl-methyl-3′,4′-epoxycyclohexane carboxylate have been used to crosslink with polyols (especially ϵ-caprolactone derived polyols). These reactions are generally catalysed by photolytically generated super acids which protonate the cycloaliphatic epoxide to form an activated monomer (AM)[3–5].

The reaction kinetics and mechanisms of phenyl glycidyl ethers have been studied extensively[6,7]. Typically, phenyl glycidyl ethers exhibit two major modes of reactivity[7]. The first is cross linking or curing reactions with reactive amine, hydroxyl or carboxyl groups. The second is the homopolymerization of the epoxy group. The homopolymerization can lead either to formation of low molecular weight oligomers or to formation of high molecular weight polymers, depending on the catalyst, temperature, and stoichiometry[7,8]. The relative extent of the homopolymerization *versus* the crosslinking reactions strongly affect the network structures, morphology, and ultimately the performance of the cross linked product(s)[7]. The mechanism of the homopolymerization of phenyl glycidyl ethers has been studied[9–11], and is generally initiated by tertiary amines. The initial step in the homopolymerization is the formation of a tertiary amine-epoxide zwitterion. The zwitterion (the negatively charged oxygen) then attacks another epoxy ring to form an oligomer via an anionic step growth mechanism. if there are no other competing reactions, the homopolymerization of the phenyl glycidyl ethers can repeat until all the epoxy groups are consumed.

In comparison with phenyl glycidyl ethers, very few kinetic and mechanistic studies have been performed on the reactions of cycloaliphatic epoxides toward hydroxyl or carboxyl functional compounds under conventional catalytic conditions. The reaction mechanisms of homopolymerization for cycloaliphatic epoxides also have not been well established[1,2]. The overall objective of our studies is to develop cycloaliphatic diepoxides as crosslinkers for waterborne acrylic coatings as previously reported[12]. This study focuses on the oligomerization of cycloaliphatic epoxides in a competitive reaction system using cyclohexene oxide (CE) in the presence of methanol (MeOH) and acetic acid (HOAc) as model compounds.

Experimental

Cyclohexene oxide (98%), methanol (99.9%), acetic acid (99.8%), triethylamine (TEA) (99.9%) and dichioroethane (DCE) (99.9%) were purchased from Aldrich Chemical Co. and were purified by distillation. Ethyl acetate (HPLC grade), hexanes (HPLC grade), diethyl ether (HPLC grade), sodium bicarbonate (GR), silica gel (Grade 922, mesh 200) and TLC (glass backed silica gel, 60 Å) were purchased from Curtin Matheson Scientific (CMS) and used as received.

A JEOL GSXFT 270 MHZ was used to record ^{1}H nuclear magnetic resonance (n.m.r.) and ^{13}C n.m.r. spectra for the products. ^{1}H n.m.r. and ^{13}C n.m.r. spectra were obtained in $CDCl_3$ with chemical shifts (δ) referenced to tetramethylsilane and $CDCl_3$, respectively. A 2020 GALAXY Series Fourier transform infra-red (*FT*i.r.) Spectrometer was used to record the i.r. spectra by directly coating the liquid sample onto KBr crystals. A Hewlett Packard (HP) 588A

* To whom correspondence should be addressed

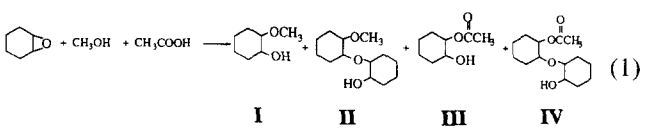
gas chromatographic (GC)-mass spectrometer was used to record mass spectra using 70 eV electron ionization. Elemental analysis was performed by Galbralth Laboratories, Inc. A HP 5890 Series II (GC) equipped with a FID Detector, HP 3396 Series II integrator, and an intermediate polar capillary column (DB17, 30 M × 0.53 mm ID, J&W Scientific) was used to analyse and record quantitative results of the reactions. The separation conditions have been reported previously[10]. The pH values of the reaction solutions were measured directly using a Corning pH Meter 320. The temperature of the reactions was controlled using a constant temperature water bath MD20 LAUDA (± 0.1°C).

The preparation of oligomers, 2-methoxy-2′-hydroxy dicyclohexyl ether (**II**) and 2-acetoxy-2′-hydroxy dicyclohexyl ether (**IV**), and the corresponding spectroscopic data of the oligomers have also been reported previously[12]. Compositions for the study of the molar ratio effect of the reactants on the product formation and distribution were varied from 1/2/2 to 6/2/2 of cyclohexene oxide/methanol/acetic acid in dichloroethane. Compositions for the reaction pathway studies for the formation of products **II** and **IV** consisted of 1 M of cyclohexene oxide with different concentrations (0.0 M, 0.1 M, 0.2 M) of *trans*-2-methoxyl cyclohexenol and *trans*-2-acetoxyl cyclohexenol with or without addition of 0.2 M of methanol and acetic acid, respectively. The compositions for the pH effect on the formation of products **II** and **IV** consisted of 2 M, 1 M and 1 M of cyclohexene oxide, methanol and acetic acid, respectively. The pH of the reaction media was varied by the addition of triethylamine. The reactions were performed at three temperatures 25°C, 35°C and 45°C to obtain the Arrhenius parameters[12].

The reagents (except cyclohexene oxide) were added to dichloroethane in a 50 ml flask equipped with a magnetic stirrer and septum. The total volume of the reactions was 10 ml. The reaction mixtures were allowed to equilibrate at a constant temperature (~5 min), and then cyclohexene oxide was transferred to the reaction flask using a syringe. All the reactions were performed in closed systems under nitrogen. At a desired time interval of the reaction, an aliquot of the reaction mixture was extracted and analyed by using GC as previously described[10,13].

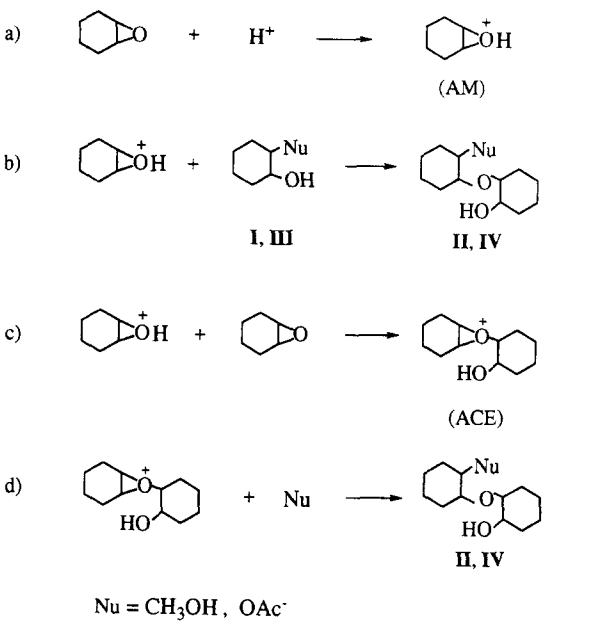
Results and discussion

Reactions of cyclohexene oxide with methanol and acetic acid gave four major products: *trans*-2-methoxyl cyclohexanol (**I**), 2-methoxy-2′-hydroxy dicyclohexyl ether (**II**), *trans*-2acetoxyl cyclohexanol (**III**) and 2-acetoxy-2′-hydroxy dicyclohexyl ether (**IV**). The structural characterizations of these products, **I**, **II**, **III** and **IV**, have been discussed in our previous studies[12]. The reaction for the formation of these products is illustrated in equation (1).



I **II** **III** **IV**

The reactions also gave rise to the corresponding tertiary ether product (2′-methoxy-2″-hydroxy tricyclohexyl-1,2-diether) and tertiary ester product (2′-acetoxy-2″-hydroxy tricyclohexyl-1,2-diether). However, the yields of these tertiary products were very low (0.2 0.5%, based on the GC analysis). Therefore, these tertiary products were not pursued in this investigation.



Nu = CH_3OH, OAc^-

Scheme 1 Possible reaction pathways for the formation of secondary Products **II** and **IV**

There were two possible competitive reaction pathways for the formation of the secondary products (**II**, **IV**) as shown in *Scheme 1*[7,14]. The first steps of the reaction pathways were the protonation of cyclohexene oxide, which has been addressed in detail previously[12]. One of the reaction pathways may occur *via* nucleophilic attack on the protonated cyclohexene oxide or the 'activated monomer' (AM) complex[5] by the primary products **I** or **III** (see *1 1b*). The other reaction pathway is the cyclohexene oxide attacking the AM, producing an extended cyclohexyl chain with an activated chain end (ACE) as shown in *Scheme 1c*[5]. The ACE of the extended cyclohexyl chain subsequently can be either terminated by methanol or acetic acid (see *1 1d*) or chain extended by addition of another cyclohexene oxide ring. The relative reactions of the ACE with the three nucleophiles are dependent on the relative nucleophilicity and the stoichiometry. For example, excess of cyclohexene oxide promotes oligomerization, whereas excess of the stronger nucleophiles effectively suppress the formation of oligomers.

In order to elucidate the most likely reaction pathway for the formation of the oligomers (the secondary products **II**, **IV**), cyclohexene oxide was allowed to react with different concentrations of each of the primary products **I** and **III**, respectively. *Figure 1* shows the formation of product **II** as a function of [**I**]. An increase in the concentration of **I** in 0.2 M increments resulted in a slight increase in the concentration of **II** (~10^{-3} M). In contrast, the addition of methanol (0.2 M) greatly enhanced the formation of **II**. Thus, the reaction pathway *via* the attack on cyclohexene oxide by primary product **I** did not substantially contribute to the formation of **II** (see *Scheme 1b*). The major reaction pathway for the formation of **II** was the oligomerization of cyclohexene oxide which was terminated by the attack of the nucleophile methanol (See *Scheme 1c* and *d*).

Figure 2 shows the variation of product concentration of **IV** as a function of [**III**]. Similar to **II**, the addition of primary product **III** to the reaction mixture did not appear to significantly increase the formation of **IV**. A two-fold increase in the concentration of **III** (0.2 M) resulted in a minimal increase in the concentration of **IV**. From this

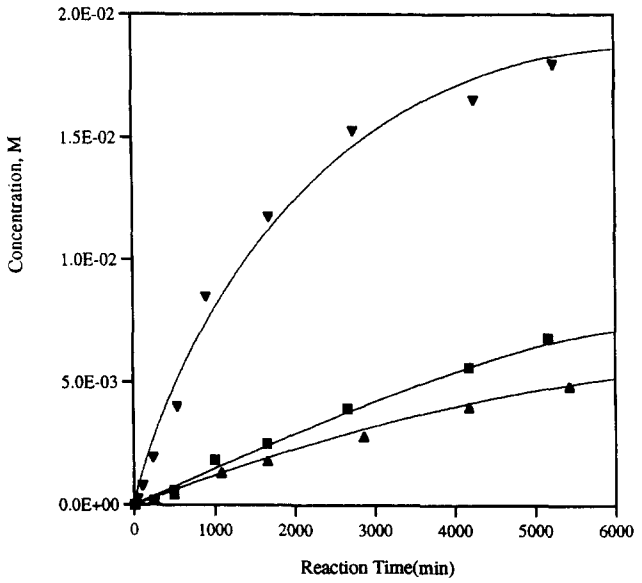


Figure 1 Formation of **II** as a function of *trans*-2-methoxyl cyclohexanol (**I**): (▼), addition of 0.2 M methanol; (■), addition of 0.4 M product **I**; (▲), addition of 0.2 M Product **I**

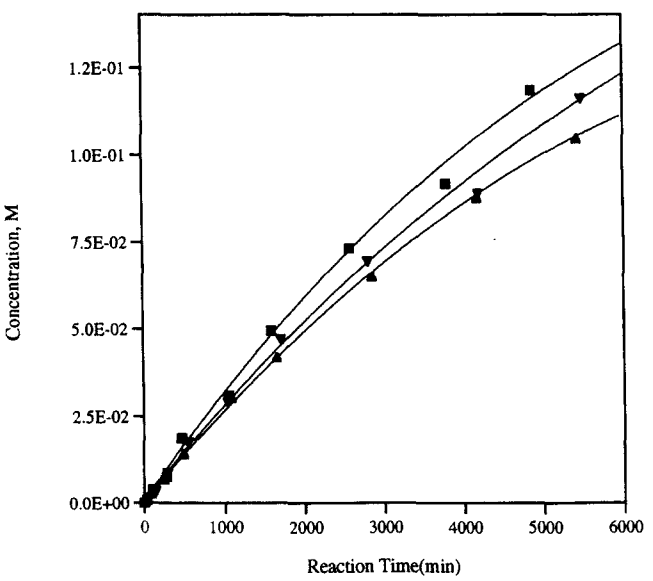


Figure 2 Formation of **IV** as a function of *trans*-2-acetoxyl cyclohexanol (**III**): (■), addition of 0.4 M product **III**; (▼), addition of 0.2 M product **III**; (▲), without wddition

result, it can be surmised that the reaction pathway did not proceed through attack by primary product **III**, as shown in *1 1b*. This can be attributed to the steric hindrance of the regenerated hydroxyl groups on the cyclohexyl ring (secondary alcohols)[15]. Thus, the major reaction pathway for both **II** and **IV** proceeds *via* the oligomerization of cyclohexene oxide and subsequent termination by a nucleophile (methanol, or acetate anion).

The relative product formation was affected by the stoichiometry of the reactants. The relative concentrations of products **I**, **II**, **III** and **IV**, as functions of the molar ratios of the reactants, are summarized in *Table 1*. The formation of products **II** and **IV** significantly increased as the molar ratio of cyclohexene oxide was increased. This is consistent with the proposed reaction pathways for the formation of **II** and **IV** in which the reaction rates showed a high order dependence on the concentration of cyclohexene oxide for

Table 1 Relative concentration of each of the products in the reaction system at pH 2.02 after 42 h

Molar ratio [CE]/[MeOH]/[HOAc]	**I** (%)	**II** (%)	**III** (%)	**IV** (%)
1/2/2	60.99	3.78	31.42	3.81
4/2/2	40.31	6.64	23.62	25.30
6/2/2	29.21	14.44	18.64	37.71

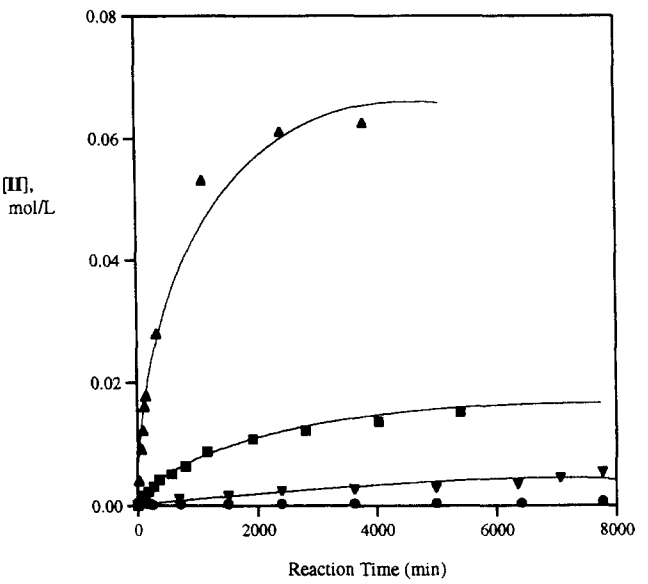


Figure 3 Formation of secondary ether products (**II**) as a function of pH and reaction time at 35°C: (▲), at pH 2.03; (■), at pH 4.55; (▼), at pH 6.16; (●), at pH 7.35

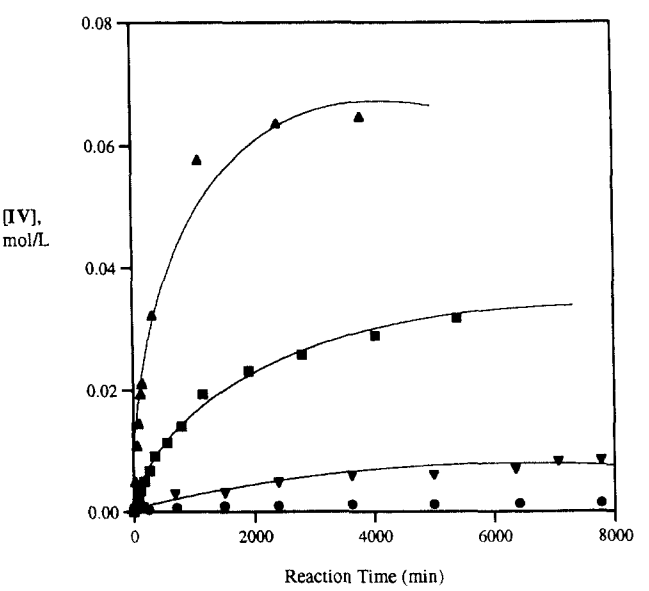


Figure 4 Formation of secondary ester products (**IV**) as a function of pH and reaction time at 35°C: (▲), at pH 2.03; (■), at pH 4.55; (▼), at pH 6.16; (●), at pH 7.35

II and **IV**. In comparison with **II**, the greater percentage for the formation of **IV** can be attributable to the greater nucleophilicity of the acetate anion[15]. In addition, the formation of **II** and **IV** was also strongly affected by the acidity of the reaction media. *Figures 3 and 4* show the pH effects on the formation of **II** and **IV**. The concentration of both products increased as the pH decreased from 6.16 to 2.03. Furthermore, no appreciable amount of **III** and **IV** was

Table 2 Summary of Arrhenius Parameters for **II** and **IV**

Product	**II**	**IV**
k_{obs} (at pH 4.4–7.3)	$2.1 \pm 0.9 \times 10^{-7}$, 45°C	$8.4 \pm 1.3 \times 10^{-7}$, 45°C
	$8.0 \pm 0.6 \times 10^{-8}$, 35°C	$3.1 \pm 0.8 \times 10^{-7}$, 35°C
	$1.9 \pm 0.8 \times 10^{-8}$, 25°C	$1.1 \pm 0.5 \times 10^{-7}$, 25°C
E_a (kJ mol^{-1})	95 ± 9	80 ± 6
Frequency factor (l^{3}mol^{-3} × min)	$1.0 \pm 0.4 \times 10^9$	$1.1 \pm 0.2 \times 10^7$

observed at pH higher than 6.16. These results suggest that the reactions for the formation of both **II** and **IV** are acid-catalysed.

It has been shown that the rate of the formation of **II** and **IV** is dependent on the concentration of cyclohexene oxide, methanol, acetic acid, and pH[13]. The corresponding reaction orders were determined by varying the concentration of one component, while keeping the concentrations of the other components in large excess. From the data, the reaction rates for the formation of **II** and **IV** were observed to be second order in cyclohexene oxide concentration, and first order in the nucleophile and acid concentration. The corresponding rate equations for the formation of the products can be expressed as follows:

$$\frac{d[\mathbf{II}]}{dt} = k_{obs,\,\mathbf{II}} \times [CE]^2 \times [MeOH] \times [H^+] \quad (2)$$

$$\frac{d[\mathbf{IV}]}{dt} = k_{obs,\,\mathbf{IV}} \times [CE]^2 \times [HOAc] \quad (3)$$

The observed rate constants for the formations of the products were obtained from the intercepts by plotting the logarithm of the formation rate as a function of the logarithm of the acid concentration. The activation energies and Arrhenius frequency factors were obtained as previously reported[12], and the results are summarized in *Table 2*. The rate constants for **IV**, at all the three temperatures, are much greater than that for **II**, and the corresponding activation energy is also lower than that for **II** (see *Table 2*). These results further reiterate that the acetate anion is a better nucleophile than methanol under the reaction conditions studied.

Conclusion

The reaction of cyclohexene oxide with methanol and acetic acid provided a mechanistic insight to the oligomerization of cyclohexene oxide. The formation of the oligomer products **II** and **IV** were strongly dependent on the stoichiometry of the reactants and the pH of the media. High relative concentrations of cyclohexene oxide and low pH favoured the formation of the model oligomer products. The major reaction pathways for the formation of these products were the chain extension of cyclohexene oxide with activated chain ends, which were subsequently terminated by a nucleophile (methanol or acetic acid). The kinetic data and the Arrhenius parameters indicate that acetic acid in the form of the acetate anion terminates the oligomerization reaction more efficiently than methanol.

Acknowledgements

The authors gratefully acknowledge the National Science Foundation (NSF)-Coatings Research Center for funding this project. The authors also wish to thank Dr Pu for the usage of the GC.

References

1. (a) Crivello, J. V. and Varlemann, U., *J. Polym. Sci. Part A*, 1995, **33**, 2463–2471; (b) Tokizawa, M., Okada, H., Wakabayashi, N. and Kimura, T., *J. Applied Polym. Sci.*, 1993, **50**, 627–635.
2. (a) Monte, D., Galia, M., Cadiz, V., Mantecon, A. and Serra, A., *Makromol. Chem.*, 1995, **199**, 1051–1061; (b) Tokizawa, M., Okada, H., Wakabayashi, N., Kimura, T. and Fukutani, H., *J. Applied Polym. Sci.*, 1993, **50**, 627–635.
3. Eaton, R. F., Golderg, D., Hanrahan, B. D., Mayer, W. P., Smith, D. F. and Soon, T. C., *Surface Coatings Australia*, 1992, **5**, 6–18.
4. (a) Decker, C. and Moussa, K., *J. Polym. Sci., Part A*, 1990, **28**, 3429–3443; (b) Egger, N., Schmidt-Rohr, K., Blumich, B., Domke, W.- D. and Stapp, B., *J. Applied Polym. Sci.*, 1992, **44**, 289–295.
5. (a) Brzezinska, K., Szymanski, R., Kubisa, P., Penczek, S., *Makromol. Chem., Rapid Commun.*, 1986, **7**, 1; (b) Penczek, S., Kubisa, P., Matyjaszewski, K., Szymanski, R., in *Cationic Polymerization and Related Processes*, ed. E. J. Goethals. Academic Press, New York, 1984, p. 139; (c) Bednarek, M., Kubisa, P., Penczek, S., *Macromol Symp.*, 1996, **107**, 139.
6. (a) Barton, J., *Adv. Polym. Sci.*, Springer-Verlag, Berlin, 1985, Vol. 72, p. 111; (b) John, N. A., George, G. A., *Prog. Polym. Sci.*, 1994, **19**, 755–795.
7. Salamone, J. C. and Riffle J. S., *Contemporary Topics in Polym. Sci.* Plenum, New York, Vol. 7, 1992, p. 103–159.
8. Younes, M., Wartewig, S. and Ledlinger, D., *Polymer*, 1994, **35**, (**24**), 5269–5278.
9. Gagnebien, D. and Madec, P. J., *Eur. Polym. J.*, 1985, **21**(3), 273.
10. Han, J. L., Hsieh, K. H. and Chiu, W. Y., *J. Appl. Polym. Sci.*, 1993, **50**, 1099–1106.
11. Rozenberg, B. A., *Adv. Polym. Sci.*, Vol. 75. Springer Verlag, Berlin, 1985, p. 111.
12. (a) Wu, S., Soucek, M. D., *Polymer*, in press; (b) Wu, S. and Soucek, M. D., *Polymer Preprints*, 1996, **37**, 2.
13. (a) Wu, S. and Soucek, M. D., *J. Coat. Tech.*, 1997, **721**, 54; (b) Wu, S. and Soucek, M.D., *Polymer Preprints*, 1996, **37**, 2.
14. Wicks, Z. W., Jones, F. N. and Pappas, S. P., *Organic Coatings: Science and Technology*, Vol. 1. John Wiley, New York, 1992, Chap. 11.
15. March, J., *Adv. Org. Chem*, 4th edn. John Wiley, New York, 1992, Chap. 6 and 8.