

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>

Alternating Copolymerization of 3,4-Epoxy-1-Butene and Derivatives with Maleic Anhydride

S. Richard Turner^a; Stephen N. Falling^a; Richard W. Blevins^b

^a Research Laboratories, Eastman Chemical Company, Kingsport, TN ^b Research Laboratories, Eastman Kodak Company, Rochester, NY

To cite this Article Turner, S. Richard , Falling, Stephen N. and Blevins, Richard W.(1997) 'Alternating Copolymerization of 3,4-Epoxy-1-Butene and Derivatives with Maleic Anhydride', *Journal of Macromolecular Science, Part A*, 34: 10, 1857 – 1866

To link to this Article: DOI: 10.1080/10601329708010313

URL: <http://dx.doi.org/10.1080/10601329708010313>

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.

ALTERNATING COPOLYMERIZATION OF 3,4-EPOXY-1-BUTENE AND DERIVATIVES WITH MALEIC ANHYDRIDE

S. Richard Turner* and **Stephen N. Falling**

Research Laboratories
Eastman Chemical Company
Kingsport, TN 37662

Richard W. Blevins

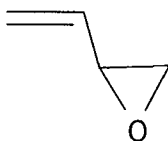
Research Laboratories
Eastman Kodak Company
Rochester, NY 14650

ABSTRACT

3,4-Epoxy-1-butene (**I**), prepared by the selective oxidation of buta-1,3-diene, is an unusual difunctional monomer containing polymerizable vinyl and epoxy groups. As expected, free radical homopolymerization of **I** and its cyclic ketal derivatives was found to be very sluggish, as expected, for the allylic monomer structures. However, **I** was found to form alternating copolymers with maleic anhydride with both 1,2- and 1,5- enchainment observed. The structures of the alternating copolymers were observed to be solvent dependent with the *in situ* formation of cyclic ketals and their incorporation into the copolymers in polymerizations done in ketone solvents. Various cyclic ketal monomers derived from **I** readily formed alternating copolymers with maleic anhydride. Thermally activated self-crosslinking of these resins was observed.

INTRODUCTION

3,4-Epoxy-1-butene (I) is a chemical intermediate and monomer which can be prepared on the commodity scale by the selective gas phase oxidation of butadiene with a supported silver catalyst [1]. This compound is a starting material for many valuable industrial intermediates and products [2]. I is also an interesting difunctional monomer containing polymerizable vinyl and epoxy groups. This report describes our studies on the free radical homopolymerization and copolymerization behavior of I and selected derivatives of I [3].



I

EXPERIMENTAL

3,4-Epoxy-1-butene- (I)

This monomer was obtained from a pilot plant process based on the selective oxidation of butadiene (1). I was purified by distillation at 65-66°C to give 99.97% purity by GC.

Maleic anhydride

This monomer was recrystallized from chloroform and then sublimed to minimize the presence of maleic acid.

N-phenylmaleimide

This monomer was obtained from Aldrich and recrystallized from ethanol before use.

Reagent grade acetone, methyl ethyl ketone, cyclohexanone, toluene, and tetrahydrofuran were used as received.

Polymer molecular weights were determined by SEC in THF using three 500 Angstrom nominal small pore ultrastyrigel columns which were calibrated with polystyrene standards. Titration of anhydride units was done by dissolving the polymer sample in 5 ml of THF. Aqueous 0.17 M sodium hydroxide was added to

cause complete hydrolysis of the anhydride units. The sample was stirred for 16 hours in a capped vial and the residual sodium hydroxide was determined by titration with hydrochloric acid. The consumed sodium hydroxide provided the measure of the total acid content.

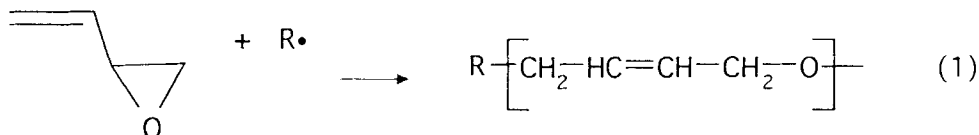
Carbon and proton NMR spectra were obtained on a GE 2E 300 MHZ instrument.

General Polymerization Procedure

Copolymerizations were done in capped Claisen polymerization bottles. The bottles were charged with the monomers, for small scale runs 1-5 g, initiator and solvent in a dry glove box under helium or the charged bottles were purged with Argon for 2 minutes to remove oxygen. The bottles were sealed with a septum and metal cap. The bottle was immersed in an oil bath at the appropriate temperature. Polymer was isolated by diluting the polymerization mixture with THF or acetone and precipitating into a non-solvent such as hexane or ethyl ether. The products were generally white or slightly off-white solids.

RESULTS AND DISCUSSION

I was found to be a relatively inert monomer under conventional solution and bulk homopolymerization conditions. No viscosity increases or precipitates were observed from attempted solution and neat free radical homopolymerizations of **I** with AIBN. Bulk homopolymerizations, with polymerization times of 24 hours at 60°C, yielded small amounts (less than 1% isolated) of an oily oligomer obtained after evaporation of the unreacted **I**. Proton NMR showed the absence of the epoxy ring and the presence of vinyl protons. The spectra were consistent with a 1,5- free radical ring-opening reaction as shown in Equation 1.

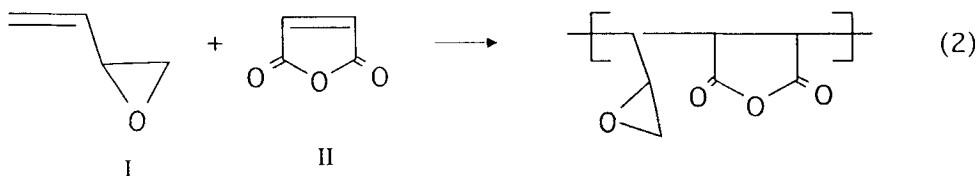


Attempted free radical copolymerization of **I** with methyl methacrylate and styrene in solution, bulk, and emulsion showed no incorporation of **I** and no apparent effect on the conversion or molecular weight of the polymers formed.

Many allylic monomers and olefin containing monomers that are sluggish or that do not polymerize under common free radical polymerization conditions

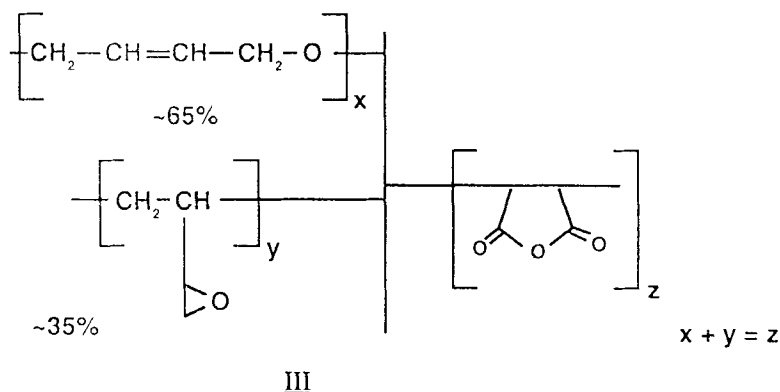
readily form alternating copolymers [4]. A well known example of this behavior is the alternating copolymerization of stilbene and maleic anhydride (**II**). Neither monomer will undergo homopolymerization using common free radical initiating systems. However, they readily undergo alternating free radical copolymerization to high molecular weight and high yield products [5]. Propylene maleic anhydride and ethylene maleic anhydride are examples of alternating copolymers of maleic anhydride that are readily formed under radical conditions [6].

Thus, we have investigated the alternating copolymerization behavior of **I** and **II**. The desired product, a polymer containing pendant epoxide and anhydride units is shown in Equation 2. Such a highly functional structure would be an interesting polymer substrate for post polymerization modification reactions and potentially useful as a polymeric crosslinker.



Our investigation of the copolymerization of **I** and **II** showed that it was initiated by conventional radical initiators such as AIBN and benzoyl peroxide. The copolymerization shut down in the presence of free radical inhibitors such as cuprous chloride. Unexpectedly, the structure of the copolymer and the yields and molecular weights were found to be very solvent dependent. Copolymerization done in THF gave the expected 1:1 ratio of **I** and **II**. However, NMR analysis clearly showed that the structure was not that shown in Equation 2. The ^1H spectrum showed resonances at $\delta 5.2$ - 5.9 which are unsaturated protons and weak resonances at $\delta 2.4$ - 3.4 which arise from residual protons of the epoxide functional group. These are slightly shifted downfield from the epoxy protons in **I**. The ^{13}C spectrum also confirms the presence of the unsaturated carbons (126-138 PPM), carbons on the epoxide (45 and 52 PPM), and a broad carbonyl resonance (170-180 PPM). The broadness of the carbonyl region arises because of several different chemical environments for the carbonyls. A portion of the anhydride is opened to the acid functions and both the acid and anhydride carbonyls can be located next to a 1,5-ring opened unit or next to an unopened epoxide. In addition the 1,5-ring opened structure appears to be a mixture of *cis* and *trans* double bonds at $\delta 5.2$ and $\delta 5.7$, respectively. Thus, for copolymerizations done in THF, the evidence is strong that both 1,5- and 1,2- propagation of **I** with **II** lead to the oligomeric products (**III**) that

are formed. An approximate ratio of 65% 1,5- to 35% 1,2- propagation was estimated from the proton NMR spectrum. Overlapping resonances and poor resolution observed in these oligomers made quantitative determination of the amount of 1,5- and 1,2- propagation difficult. Although free radical ring opening polymerizations are well documented with monomers such as vinyl cyclopropanes [7], this appears to be the first observation of participation of a free radical ring opening monomer in alternating copolymerization.



The GPC number average molecular weight of the oligomers was in the 1000 range and was insensitive to the initiator concentration whereas the yield increased with initiator (Figure 1). These observations most likely arise from high levels of chain transfer with the allylic monomer and unsaturated oligomer chains.

The copolymer formed in ketone solvents was more complicated and the structure was unexpected. NMR analysis and compositional analysis by titration of the anhydride groups showed that the composition contained less than 50 mol% anhydride units over a wide feed ratio of monomers. The titration composition plot is shown in Figure 2. The copolymerization was followed by NMR by doing the reaction in a sealed NMR tube. A control polymerization, in acetone solvent, without free radical initiator showed the formation of a new low molecular weight compound and the loss of the epoxide function. Subsequent NMR and GC/MS analyses identified this small molecule as the dioxolane addition product (IV) of 2-butanone and I. Similar products were observed in other ketone solvents such as acetone and cyclohexanone. These dioxolane products were also observed when rigorous drying conditions were used for the reactants and solvents. Maleic anhydride, for example, was recrystallized and sublimed to remove residual maleic acid. The dioxolanes formed both thermally in the absence and in the presence of the free radical initiator and thermally when a free radical inhibitor was present. When N-

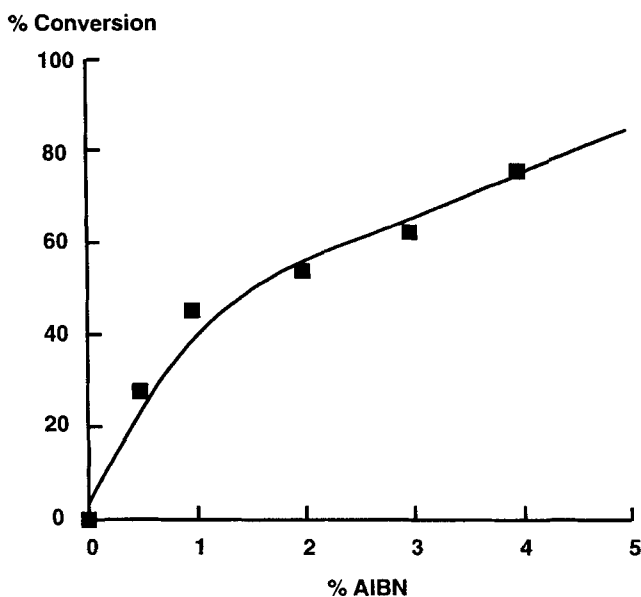


Figure 1. Polymer yield of copolymerization of I and II at 60°C in THF with AIBN as the initiator. The M_n , as determined by GPC, remained approximately 1000 over the entire initiator concentration range.

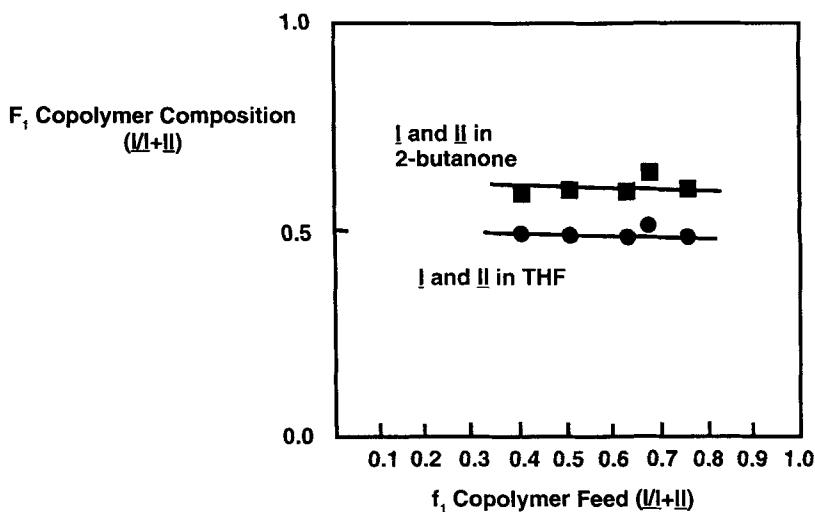
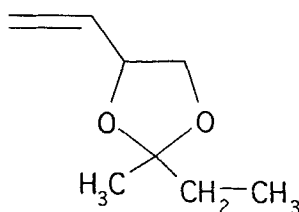
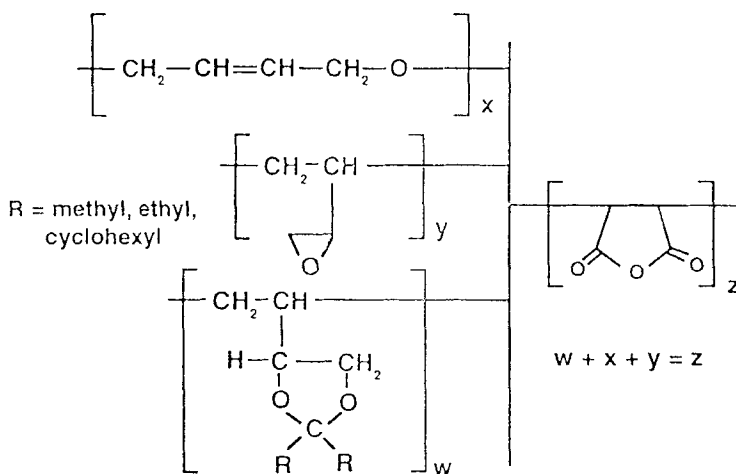


Figure 2. The copolymer composition curve for the copolymerization of I and II for copolymerizations done in 2-butanone and THF at 60°C with AIBN as initiator.

phenylmaleimide was substituted for maleic anhydride, no dioxolanes were observed during copolymerization with I. This suggests that formation of the dioxolanes results from acid catalyzed addition of the ketone to I and not from an unknown free radical cyclization reaction. Thus, it is likely that either a small amount of maleic acid remains in the purified maleic anhydride or a small amount of adventitious water in the ketone solvents forms some maleic acid which catalyzes the adduct formation. Thus, the structures of the copolymers formed in ketone solvents can be represented by the structure shown in V. Poor resolution and overlapping resonances prohibited reasonable estimates of the ratios of the comonomers in the final product.



IV



V

The dioxolane adducts were found to be very active as comonomers with II. The alternating copolymerization of IV and II readily yielded copolymers of modest molecular weights with a strictly alternating structure as determined by NMR. A plot of M_n vs. the inverse of the square root of the initiator concentration (Figure 3) shows the expected linear behavior. GPC number average molecular weights

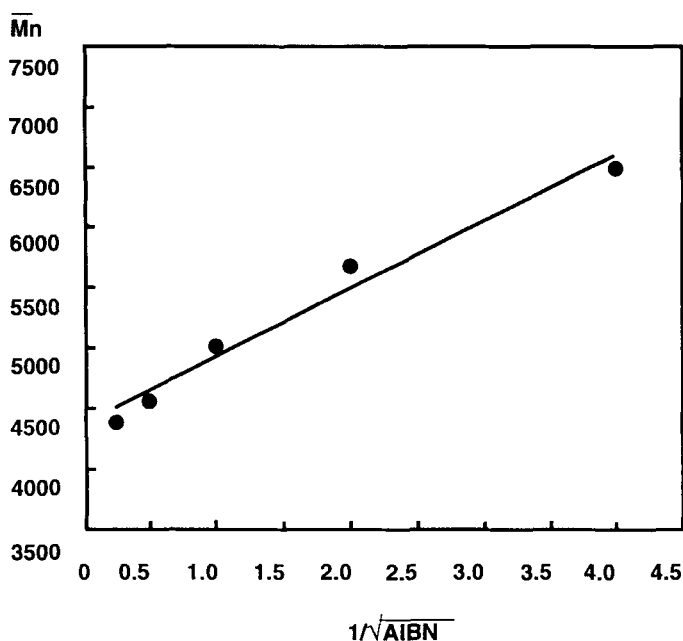
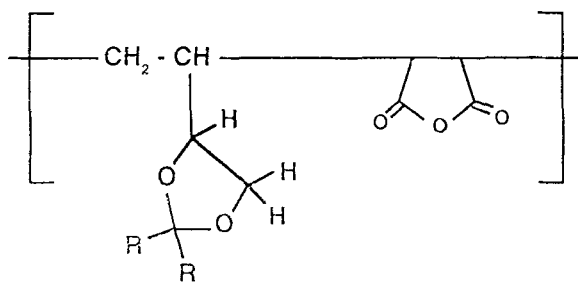


Figure 3. Number average molecular weight vs. $1/\text{AIBN}$ for the copolymerization of IV and II done in 2-butanone at 60°C with AIBN as initiator.

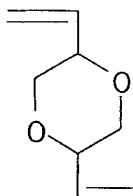
greater than 5,000 were readily obtained with molecular weight distribution around 2.5. Titration and NMR analyses confirmed the 1:1 composition (VI). These copolymerizations could be done in ether, ketone, or non polar solvents such as toluene. It was also possible to do these copolymerizations in an excess of the dioxolane as solvent.



VI

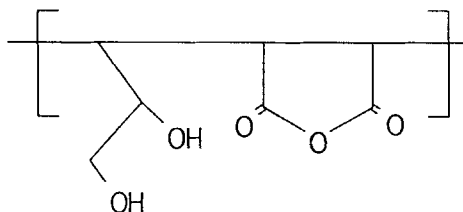
When the copolymerization of I and II were done in non-polar solvents such as toluene or in the absence of solvent crosslinked polymers were obtained. We

observed the formation of the cyclic dimer (VII) of I by GC/MS when I and II were heated together in the absence of a free radical initiator. An authentic sample of VII added to a copolymerization of I and II in acetone gave a crosslinked polymer. Therefore, we believe that the crosslinked polymers results from the *in situ* formation of VII which acts as a crosslinking agent, through the 2 allylic groups, in the copolymerization.

VII

The copolymers of I and II prepared in ether or ketone solvents were soluble in a large number of organic solvents including methanol, ethanol, isopropanol, acetone, 2-butanone, THF, dioxane, and DMF *inter alia*. The copolymers were also soluble in 5% aqueous NaOH and 5% aqueous HCl. The copolymers were insoluble in water, heptane, toluene, chloroform, dichloromethane, ethyl acetate, and acetonitrile *inter alia*. The copolymers of the dioxolane monomers and II showed similar solubilities.

The copolymers of II and the dioxolane such as V appear be latent thermally crosslinkable materials. Heating a film of a copolymer of V and II to temperatures under 100°C did not change the solubility of the film. At temperatures of greater than 150°C, the films became insoluble. When heated to 150°C, the copolymers showed a large weight loss by TGA. Mass spectral analysis showed that a large component of the gas evolved was the parent ketone from the dioxolane. This suggests a step-wise loss of the ketone and then subsequent crosslinking of the resultant pendant diols with the anhydride groups. The structure of the diol polymer is shown in VIII.

VIII

CONCLUSION

Free radical polymerization studies of **I** showed that it has a propensity to undergo ring opening radical reactions to add both in a 1,2- and 1,5- mode. Free radical copolymerization with **II** was found to be solvent dependent with the allylic reaction products of **I** with solvent or itself becoming incorporated into the copolymer structure.

Whereas, **I** copolymerized with **II** to form relatively low molecular weight oligomers under solution free radical conditions, the dioxolane derivatives of **I** with ketones, were more active monomers and resulted in alternating copolymers with number average molecular weights of over 5000. The resulting polymers were thermally crosslinkable with the release of the ketone from which the dioxolane was derived.

REFERENCES

- [1] J. R. Monnier and P. J. Muehlbauer, U.S. Pat. 4,950,773, (1990) (to Eastman Chemical Company).
- [2] C & E News, August 21, 1995, p. 7.
- [3] R. W. Blevins and S. R. Turner, U.S. Pats. 5,013, 806 (1991); 5,019,635 (1991); 5,071,930 (1991); 5,071,931 (1991); 5,071,932 (1991); and 5,077,365 (1991) (to Eastman Chemical Company).
- [4] J. M. G. Cowie, Ed., *Alternating Copolymers*, Plenum Press, New York (1985).
- [5] M. L. Hallensleben, *Eur. Polym. J.*, 9, (3), 227-31 (1973).
- [6] B. C. Trivedi and B. M. Culbertson, *Maleic Anhydride*, Plenum Press, New York (1982).
- [7] T. Endo and K. Suga, *J. Polym. Sci., Polym. Chem. Ed.*, 27, 1831 (1989).