

Torsional Braid as a Kinetic Tool for the Study of the Polymerization of Viscous Materials. II. Catalytic Effects in the Polymerization of Carboxylic Acid-Terminated Polybutadiene Prepolymers with Tris[1-(2-methyl)aziridinyl]phosphine Oxide

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Synopsis

The torsional braid technique for studying the polymerization of viscous substances has been extended to a study of the homogenous catalytic behavior of a number of acidic and basic catalysts in the polymerization of carboxy-terminated polybutadiene with tris(methyl aziridinyl)phosphine oxide. No general catalytic behavior was observed. Specific catalysis was observed in the case of lithium oleate, where the gel time was decreased, and in the case of bis(tri-*n*-butyltin) oxide, where the gel time was increased. The average energy of activation for all of these polymerizations was 13.9 ± 0.5 kcal./mole. This energy of activation and the reaction environment, when compared with the data in the literature, strongly suggest that the explanation that a change in the rate-determining step occurs as a function of the polarity of the reaction medium fails to account for all of the results.

INTRODUCTION

The first paper¹ of this series established the usefulness of the modified torsional braid technique as a tool for the study of the kinetics of polymerization of viscous polymeric substances. Making use of this technique, the work in this paper describes the catalytic effect of several acidic and basic substances on the polymerization of carboxylic acid-terminated polybutadienes (CTPB) and tris[1-(2-methyl)aziridinyl]phosphine oxide (M-APO). In order to avoid complications caused by known proton catalysis of aziridinyl ring-opening reactions²⁻⁸ it was decided that in the selection of the acid catalysts the Lewis acids rather than Brönsted acids be used. We have studied a number of potential catalytic agents in the polymerization of a commercial carboxyl-terminated polybutadiene with a purified tris(methyl aziridinyl)phosphine oxide in order to determine the effects upon the energy of activation and upon the polymerization gel time.

EXPERIMENTAL

Torsional Braid and Rate Measurements

A description of the torsional pendulum used in these experiments and the braid-coating technique are described in a previous publication.¹ The newer version of the pendulum by Gillham,⁹ not available at the time of this investigation, would have been quite suitable. It would not have eliminated the creep problem previously discussed unless the handmade glass braid were used.

The experiments to determine the effect of the catalytic substance upon the polymerization were performed by adding 1 wt.-% of the catalyst to the rubber resin before formulating it with the crosslinking agents. In the cases where less than 1% was used, the limiting factor was the solubility of the agent in the rubber prepolymer since it was desired to eliminate heterogeneous systems. Each system was polymerized at a number of fixed temperatures. The rates at a minimum of four temperatures were used for each activation energy plot. Generally the rates at six temperatures between 50 and 90°C. were obtained.

Preparation and Analysis of Carboxylic Acid-Terminated Polybutadiene (CTPB)

The CTPB (Butarez CTL Type II lot T193, Phillips Petroleum Co., Bartlesville, Oklahoma) was used as received. The carboxylic acid content of the polymer was determined by a modified method of Sorenson.¹⁰ Alcoholic potassium hydroxide was used instead of the aqueous solution.

Preparation and Analysis of Tris[1-(2-methyl)aziridinyl]phosphine Oxide (MAPO)

The MAPO (Lot 9103) was analyzed as received by using the method¹¹ described by the manufacturer. The procedure involves a reaction with excess sodium thiosulfate under acidic conditions.

The MAPO was distilled at reduced pressure (b.p. 110–116°C., 5 torr). The distilled MAPO was analyzed according to the above procedure. The distilled MAPO was used in all polymerization experiments.

Polymerization Procedure

The CTPB-MAPO weights were so adjusted that a 1:1 equivalency of CTPB and MAPO was obtained. No adjustment was made for the weights of the dissolved catalytic agents. The mixing, impregnation and coating methods are described in Part I. The polymerization chamber was flushed with dry nitrogen preheated to the polymerization temperature. The pendulum period was measured at 30-min. intervals during the entire polymerization time of interest.

Catalytic Agents

(*N*-Methyl)morpholine (NMM). NMM (practical grade) (Eastman Organic Chemicals, Distillation Products Industries, Rochester, N. Y.) was used as received.

Bis(*tri-n*-butyltin) Oxide (TBTO). TBTO (95% min, M & T Chemicals, Inc., Rahway, N. J.) was used as received.

1-Phenyl-3-methyl-3-phospholene-1-oxide (PMPO). PMPO was prepared by Dr. R. A. Henry, Research Dept., Naval Weapons Center, China Lake, according to the procedure of Lyman and Sadri.¹²

Lithium Oleate (LO). LO was obtained as a technical grade sample (Foote Mineral Company, Exton, Pa.). LO was recrystallized twice from dry methanol and further dried under vacuum, m.p. 197–200°C, H₂O content 1.75%.

RESULTS AND DISCUSSION

In order to establish the reliability and reproducibility of our rate data, where the rate is defined as the polymerization time required to obtain a gel, a number of polymerization experiments of the CTPB-MAPO system were performed. In the previous publication¹ the results for one set of experiments were given. Figure 1 shows the Arrhenius plot for all of the "uncatalyzed" polymerizations performed with the equivalency ratio of

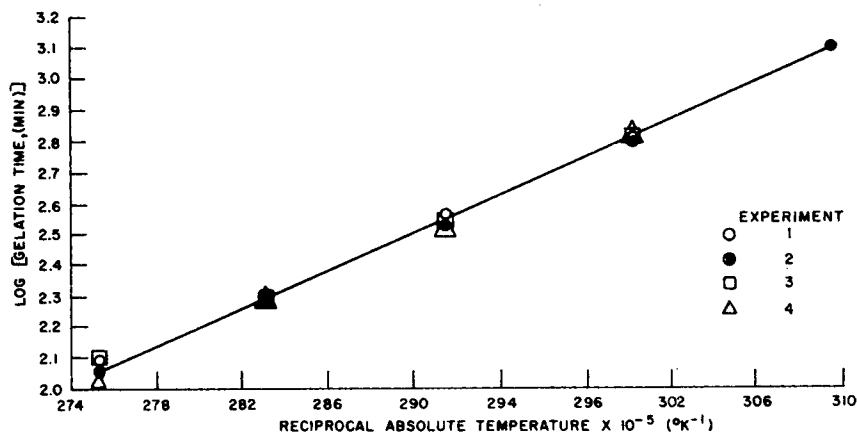


Fig. 1. Plots of activation energy for the uncatalyzed Butarez II-MAPO polymerization.

CTPB to MAPO of unity. All of the data can be described by one straight line with a slope of 13.8 ± 0.5 kcal./mole. This line and all of the subsequent curves were obtained by analyzing the data of Table I with the aid of an IBM T094EDPM computer. The method of least squares was used to determine the position of the line and its slope. The reliability of the experimental procedure is supported to some extent by the fact that some variations in mixing, braid impregnation, braid sizing, and handling

times were encountered. These variations appeared to have very little effect upon the line or its slope.

Figure 2 gives the Arrhenius equation plot for all of the catalyzed runs. The increase in activation energy E^* for the PMPO system of 1 kcal./mole is probably within the expected range of experimental error.

TABLE I
Summary of Gel Time Data for CTPB-MAPO Polymerization
at 1:1 Equivalency Ratio of CTPB to MAPO

Ex-periment	Time to gel point, min.					E^* , kcal./mole
	90°C.	80°C.	70°C.	60°C.	50°C.	
1	120	202	370	650		13.6
2	114	199	333	630	1250	13.9
3	122	197	344	640		13.3
4	104	201	330	660		14.5

In Table II the data on the gel times of all of the catalyzed systems at 70°C are given.

From the data in Table II it is apparent that the gel time is strongly affected by the nature of the additive in a manner that appears to be

TABLE II
Gel Times and Activation Energies for CTPB-MAPO-Catalyst System

Catalyst	Time to gelation, min.					Related figures	E^* , kcal./mole
	90°C.	80°C.	70°C.	60°C.	50°C.		
None ^a	115	200	344	645	1250	1	13.8
TBTO	173	278	485	960		2	13.7
NMM	125	225	385	650		2	13.2
NMM	120	209	365	660		2	13.6
PMPO	122	211	372	665	1620	2	14.8
LO (0.5%) ^b	73	146	272	519	1035	2	14.6

^a Average of four experiments.

^b Interpolated values.

opposite to the fashion that would be predicted from the activation energy plot. This would tend to indicate that the catalytic agent has little effect upon the rate-controlling step in the carboxy-MAPO reaction and suggests that either some other chemistry is involved in the retardation exhibited by TBTO and the acceleration exhibited by LO or that the frequency factor in the rate determining step is altered. Attempts to determine whether some of the components are being removed from the reaction by coordination or complex formation in the case of TBTO through the use of infrared absorption failed to show change in the absorption of either CTPB or MAPO upon the addition of TBTO.

In the case of LO it was found that the greatest effect the water content appears to have upon the resin system is upon the solubility of LO in the liquid rubber. At the measured water content of 1.75% about 0.28 mole of water is present for each mole of LO. Earlier experiments with less dry LO indicated a similar decrease in the gel time, demonstrating that the observed effect is not a function of the water content. These latter experiments gave similar kinetic plots but were not included because some of the LO failed to go into solution and it was desired to avoid complications of heterogeneity.

In a series of reactions with the model compounds of MAPO and propanoic acid, LO and lithium chloride have been found to increase the rate of reaction. Unfortunately, insufficient experiments were conducted to permit the detailed determination of the kinetics and energies of activation.

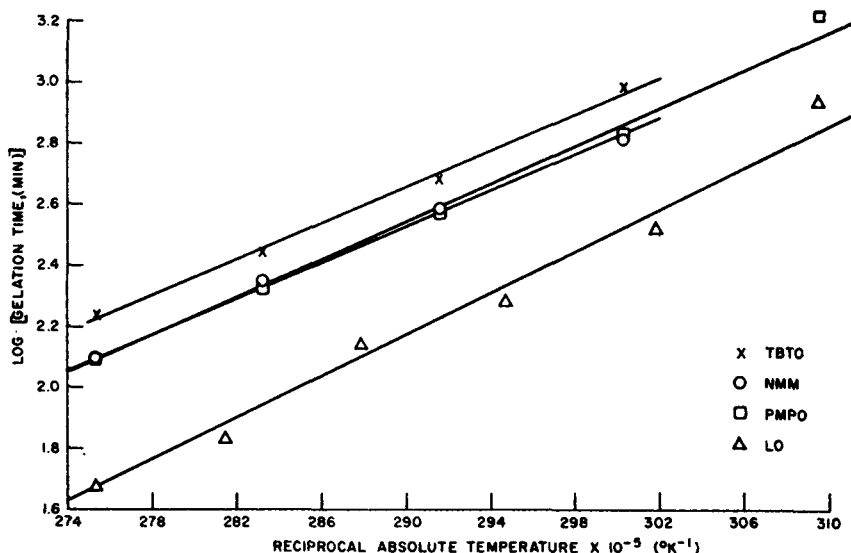
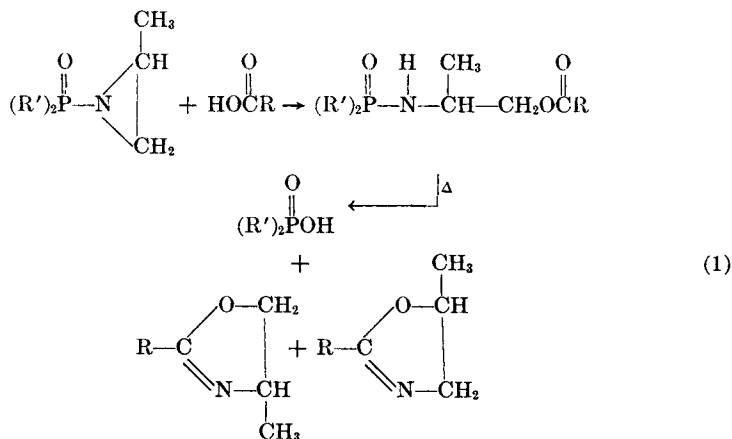


Fig. 2. Plots of activation energy for the catalyzed Butarez II-MAPO polymerization.

It is of interest that the strong base NMM failed to have an effect upon the polymerization in view of the fact that in kinetic studies with model compounds reaction was found to be second-order with respect to carboxyl acid group.¹³ One might expect that the strong base would change the carboxylic acid concentration in the system, thereby lowering the rate. No such effect was observed.

An attempt was made, with the use of NMR (nuclear magnetic resonance) as the analytical tool to determine whether the lithium salt affects the mode of addition of the acid to the imine. The product formed on the addition of propanoic acid to MAPO at room temperature with the lithium salt present was found to be the same as that formed without the lithium salt

present. This product was the tris[*N*(1-methyl-2-propionyloxy)ethyl]-phosphoramidate. No attempt was made to examine the amount or type of oxazoline that may have been formed during the reaction. The fact that oxazolines indicated by eq. (1)



where $\text{R}' = 2\text{-methyl aziridinyl}$, $\text{R} = \text{CH}_3$ ¹³ or (CH_3CH_2) do indeed form was observed by Johnson et al.¹³ at temperatures in excess of 60°C . The formation of the oxazoline is facilitated by elevated temperatures^{2,14} so that despite the 2-5% detectability limit of the NMR it is not unexpected that under ambient conditions oxazoline formation was not indicated, while in the experiment of Johnson et al. the formation of the oxazolines was apparent.

Since the parameter measured in this paper is the time for a polymer to gel, and further since it has been demonstrated by Johnson et al. that the oxazolines which do form result in the destruction of the phosphorus-nitrogen bond, the results of this paper can be explained in terms of inhibition or acceleration of the oxazoline formation, i.e., LO may inhibit the formation of the oxazoline, while the TBTO may accelerate the reaction. Since the step involving the addition of the acid to the MAPO is probably the rate-determining step^{3,7} in the gel time experienced, subsequent reactions of the compounds formed should be expected to have very little effect upon the activation energy.

Unfortunately since absolute rate constants and orders of reaction are not obtained by this method, the entropy or frequency factor cannot be calculated.

In Table III are tabulated the energies of activation for various acid-imine reactions. The activation energies obtained in this work are not at variance with those obtained by other works. There is some indication that a solvent effect may exist and that a decrease in the energy of activation may occur with decreasing solvent polarity. The environment most comparable to that of this paper is the reaction of MAPO with acetic acid in toluene. Since the reported reactions were conducted in acetic acid

concentrations of between 0.1 and 2.0*N*, the average solvent polarity is much higher than the condition reported in this paper. Comparing the results of Johnson et al. with those of Powers et al. reveals that a substituent on the imine nitrogen seems to have little effect upon the measured activation energies. The discussion of Powers et al.⁷ suggests that the activation energy effect as a function of polarity indicates a change in the rate determining step from an addition to the immonium ion in polar media (aqueous acid systems) to a rate determining step involving the formation of immonium ion in nonpolar media (carbon tetrachloride). This explanation would not be valid for the intermediate cases of this paper, the work of Johnson et al., and the work of Powers et al.

TABLE III
Summary of Energies of Activation Data for Various Imine Reactions

Reagent	Imine	Solvent	Energy of activation, kcal./mole	Reference
Carboxy-terminated polybutadiene	MAPO	None	13.9 ± 0.5 ^a	This work
Acetic acid	MAPO	Dioxane	19.0	13
Acetic acid	MAPO	Toluene	19.0	13
Water	Ethylenimine	Aqueous perchloric acid	23.0 ± 0.6	8
Water	2-Ethyl ethylenimine	Aqueous perchloric acid	23.1 ± 0.1	8
Water	2,2-Dimethyl ethylenimine	Aqueous perchloric acid	24.3 ± 0.4	8
Water	2-Ethyl ethylenimine	Aqueous hydrochloric acid	24.1	5
Hydrochloric acid	2-Ethyl ethylenimine	Aqueous hydrochloric acid	22.7	5
Benzoic acid	2-Ethyl ethylenimine	Dioxane	17.0	7
<i>p</i> -Nitrobenzoic acid	2-Ethyl ethylenimine	Dioxane	16.8	7
Thiophenol	2-Ethyl ethylenimine	Carbon tetrachloride	11.0	3,7

^a Average of all experiments reported in this paper.

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