Polymerization Kinetics and Technology

NORBERT A. J. PLATZER

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Polymerization Kinetics and Technology

Norbert A. J. Platzer, *Editor*

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Robert F. Gould, *Editor*

FOREWORD

ADVANCES IN CHEMISTRY SERIES was founded in 1949 by the American Chemical Society as an outlet for symposia and collections of data in special areas of topical interest that could not be accommodated in the Society's journals. It provides a medium for symposia that would otherwise be fragmented, their papers distributed among several journals or not published at all. Papers are refereed critically according to ACS editorial standards and receive the careful attention and processing characteristic of ACS publications. Papers published in ADVANCES IN CHEMISTRY SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

PREFACE

At current projections the world's population will double in the next 30 years. World production of synthetic polymers, however, is doubling every five years according to an annual growth rate of 15.6%. During the 1960's, U.S. polymer production showed an annual gain of 14.5% while the rest of the chemical industry expanded at an annual rate of only 9%. This made synthetic polymers the fastest growing area in chemical industry. During the same period the growth rate of world polymer production exceeded the domestic rate and amounted to an average of 16.6% per year.

The growth rate of polymer production is determined by two factors: demand and technology. Demand depends on economy. In 1970 domestic production stayed at almost the 1969 level, as Figure 1 illustrates. In 1971 it grew 8%. These values represented a significant

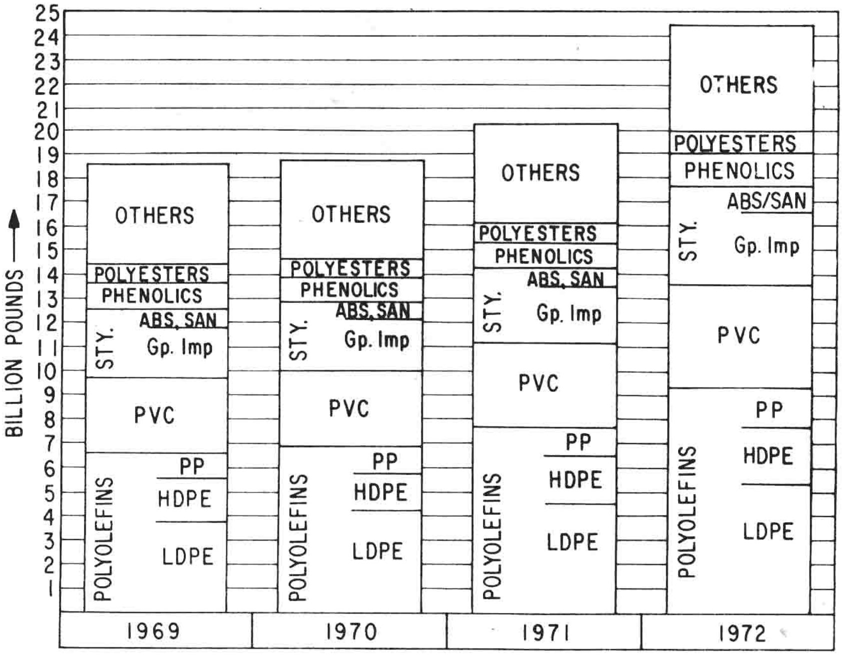

Figure 1. U.S. production of synthetic thermoplastics and thermosets

decrease, and the question arose as to whether the polymer industry had reached the plateau of saturation and maturity. The 1972 growth rate of more than 20% provided the answer: the slowdown was caused only by the general recession, and the demand for polymeric materials still exists and is rising.

Polyethylene, polypropylene, poly(vinyl chloride), styrene resins (including ABS), phenolics, and polyesters are the major commercial polymers and together represent over 80% of the total domestic production, also shown in Figure 1). The sharply increased demand in 1972 required manufacturing plants to operate at almost full capacities. Shortages may occur temporarily until new facilities are installed.

In 1950 the United States was the leading polymer manufacturer and contributed to 69% of the world's production. The economic boom in Western Europe and Japan of the 1950's and 1960's raised their productivity and reduced our world participation to 41% in 1960 and 27% today. The seven largest polymer producing countries are United States, Japan, West Germany, Italy, U.S.S.R., Great Britain, and France, as shown in Figure 2.

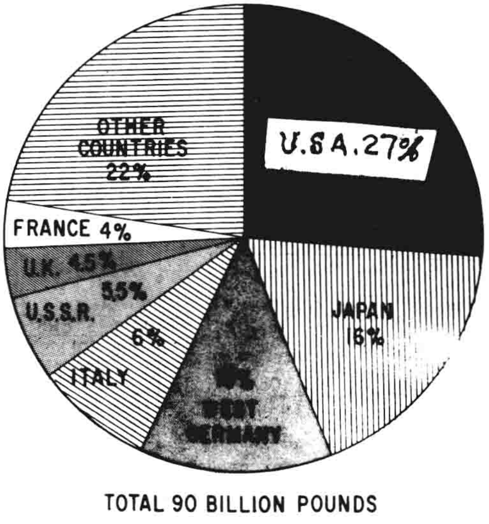

Figure 2. Participation of different countries in world production during 1972

Technology represents the second growth factor and depends on research. Poly(vinyl chloride) is the oldest of the synthetic commodity thermoplastics and has been used plasticized and rigid for 35 years. Its manufacturing technology by suspension and emulsion polymerization is known worldwide. The technology of high pressure polyethylene was developed later. Low pressure processes with Ziegler-Natta or

Phillips catalysts for linear polyethylene and polypropylene and the graft copolymerizations for impact polystyrene and ABS are even younger and have not yet spread into the less industrialized countries of world. The production of polyolefins, poly(vinyl chloride), and styrene resins on a worldwide basis as well as of all synthetic polymers is shown in Figure 3. A comparison of the U.S. production in Figure 1 and in Figure 3 demonstrates the effect of age and dissemination of technology. It shows that relatively more poly(vinyl chloride) but less polyolefins and styrene resins are produced worldwide than in this country.

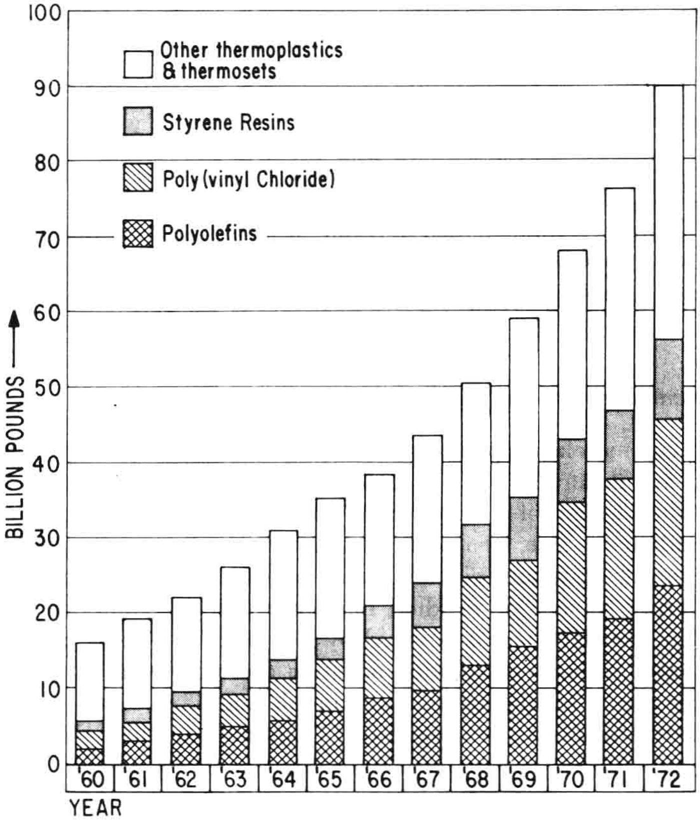

Figure 3. World production of plastics

With the growth of the polymer industry, competition has become fiercer and selling prices lower. In view of the competitive situation, priorities of industrial research have changed. It has become imperative to produce the same commodity polymers with better properties at reduced cost by improved processes and in larger units. To stay ahead, it is also necessary to understand the mechanism of polymerization more fully, to modify the existing commercial products, and to develop new ones.

This volume contains 18 papers on the kinetics and technology of addition and condensation polymerization processes. These papers were presented at the sixth symposium on this subject held by the Division of Industrial and Engineering Chemistry and the Division of Polymer Chemistry during the A.C.S. Meeting, Boston April 9-14, 1972. They are concerned with known commercial products. New polymers and novel polymerization reactions presented at the same symposium are collected in the companion volume, ADVANCES IN CHEMISTRY SERIES No. 129.

Polymerization Kinetics

To broaden our overall knowledge of process kinetics the first chapter of this volume deals with elementary reactions in radical and anionic polymerization; it was written by G. V. Schulz, the first recipient of the H. Staudinger Award. It is followed by a discussion on monomer constitution and stereocontrol in radical polymerization by H. G. Elias *et al.*

Equipment and Process Design

For commercial suspension and solution polymerization current batch reactors are generally 2000 to 10,000 gallons in size. G. Beckmann describes the design of larger, more economical polymerization kettles, 53,000 gallons in size, as installed at C. W. Huels, and the problems of heat removal, agitation, cleaning, and safety. The behavior of viscous melts during solvent or residual monomer stripping and the design of wiped-film devolatilizers is covered by F. Widmer. These devolatilizers can be used in mass or solution addition and condensation polymerization processes. Mechanochemical complexing is a novel method for condensation reactions developed by C. Simionescu and C. Vasilu-Oprea.

Addition Polymerization Products

To the synthetic thermoplastics and thermosets of Figure 3, the synthetic rubbers and elastomers may be added. In 1972 they amounted to more than 15 billion pounds worldwide. SBR has been the workhorse of the rubber industry since World War II. Being used in tires, it amounts to over half of all rubber production. G. M. Burnett and G. G. Cameron have investigated the way its crosslinking during polymerization affects its properties and processability. For years it has been the intention to raise the heat distortion temperature of polystyrene. One method is to copolymerize styrene with a small quantity of divinylbenzene. J. W. Breitenbach and H. Axman have studied the formation of popcorn polymers from styrene with less than 1% divinyl benzene.

Rigid impact polv(vinyl chloride) can be made either by polyblending or by grafting. P. Dreyfuss, M. P. Dreyfuss, and H. A. Tucker, discuss in their chapter polyblends of poly(vinyl chloride) with polyethers. F. Wollrab, F. Declerck, J. Dumoulin, M. Obsomer, and P. Georlette review grafting of vinyl chloride upon polyethylene, ethylene/propylene rubber, and chlorohydrin rubber.

H. Hopff and N. Balint developed a copolymerization process for tetrachloroethylene with ethylene. Radiation-induced chlorination of polyisobutylene is the subject of the chapter of C. Schneider and P. Lopour. M. Litt, V. T. Stannett, and E. Vanzo show that the polymerization of vinyl caproate follows the kinetics of styrene.

Condensation Polymerization Products

Unsaturated polyesters, primarily copolyesters of propylene glycol with maleic and phthalic acid, dissolved in styrene monomer, are used in the glass-fiber reinforced polyester market. They are cured commercially in a series of involved and expensive steps. R. D. Deanin and V. G. Dossi propose a simplified one-step curing method. Polyethylene terephthalate is manufatcured by a condensation reaction in which ethylene glycol is liberated. Diffusion and removal of the glycol from the viscous melt determine and decelerate the reaction rate. T. Shima, T. Urasaki, and I. Oka discovered that addition of a small amount of certain acid derivatives accelerates the condensation polymerization significantly, yielding a high molecular weight product of low free-acid content.

Propylene oxide is one of the raw materials used to manufacture rubbery and crystalline polyepoxides. R. J. Herold and R. A. Livigni describe propylene oxide polymerization with hexacyanometalate salt complexes as catalyst. Polyphenylene oxide is made by copper catalyzed oxidative coupling of 2,6-dimethylphenol. G. D. Cooper, J. G. Bennett, and A. Factor discuss the preparation of copolymers of PPO by oxidative coupling of dimethylphenol with methylphenylphenol and with diphenylphenol.

At our 1958 symposium, polycarbonate was introduced. Since then this polymer has reached a domestic production of 50 million pounds per year. J. T. Gregory, J. A. Cook, and A. B. Robertson report on the synthesis of polycarbonate oligomers useful in making random and block copolycarbonates.

Polyurethanes are manufactured by the reaction of diisocyanates with diols, diamines, or other organic compounds containing two or more active hydrogens. The reaction rate between a diisocyanate and alcohols catalyzed with dibutyltin dilaurate yielding urethanes was studied by G. Borkent and J. J. Van Aartsen.

The chapters in this volume will broaden our insight into polymerization kinetics and provide information technologically important on commercial processes and products. New polymers and novel polymerization reactions are covered in the 18 chapters of the companion volume.

NORBERT A. J. PLATZER

Longmeadow, Mass.
December 1972

CONTENTS

1

Elementary Reactions in Radical and Anionic Polymerizations

G. V. SCHULZ

Institut für Physikalische Chemie der Universität Mainz, West Germany

Studies of the influence of solvents on polymerization processes by stationary and nonstationary methods give the following results. In radical polymerizations, solvent viscosity mainly influences diffusion-controlled elementary reactions. The effect on efficiency demands new considerations of the cage effect. The influence on chain termination provides interesting information on segment diffusion, mutual penetration of polymer coils, and internal viscosity. In anionic polymerizations, the polarity of solvents strongly influences equilibria between three forms of the active end groups—the two kinds of ion pairs and the free carbanion. The equilibria between these forms and the corresponding enthalpy and entropy differences were determined by kinetic and conductance measurements. The influence of solvents on the rate constants of the monomer addition to each form of the active chain ends is relatively small. Analysis of molecular weight distributions gives, in addition the activation enthalpies and entropies of the transitions between these forms.

Solvents have different effects on polymerization processes. In radical polymerizations, their viscosity influences the diffusion-controlled bimolecular reactions of two radicals, such as the recombination of the initiator radicals (efficiency) or the deactivation of the radical chain ends (termination reaction). These phenomena are treated in the first section. In anionic polymerization processes, the different polarities of the solvents cause a more or less strong solvation of the counter ion. Depending on this effect, the carbanion exists in three different forms with very different propagation constants. These effects are treated in the second section. The final section shows that the kinetics of the transitions between these three forms of active chain ends can be measured by analyzing molecular-weight distributions on anionically prepared polystyrenes as a function of solvent and temperature.

Influence of Solvents on Radical Polymerization

The fundamental processes of initiation, propagation, and termination of a polymer chain can be formulated this way (transfer reactions are not considered):

$$\text{Initiation}\quad \left\{\begin{array}{l} \mathrm{R_2} \xrightarrow{k_d} \mathrm{R}\cdot \\ \left.\begin{array}{r} 2\mathrm{R}\cdot \rightarrow \mathrm{R'_2} \\ \mathrm{R}\cdot + \mathrm{M} \rightarrow \mathrm{RM}\cdot \end{array}\right\} \text{efficiency } f \end{array}\right.$$

$$\text{Propagation}\quad \mathrm{RM}_n\cdot + \mathrm{M} \xrightarrow{k_p} \mathrm{RM}\cdot_{n+1}$$

$$\text{Termination}\quad \mathrm{RM}_n\cdot + \mathrm{RM}_m\cdot \xrightarrow{k_t} \text{dead polymer}$$

The least known of these reactions is chain initiation together with the efficiency of the primary radicals. This group consists of at least three elementary reactions. The so-called cage effect certainly plays an important role. On the other hand, the cage effect in its classical form cannot explain all phenomena sufficiently.

The propagation step is a special case of the reaction of a radical with an unsaturated compound. The process can be influenced by EDA-complexes of the radical with the solvent and the monomer, as Henrici-Olivé (1) have shown. These effects are not very large.

In contrast to the propagation step, the termination process strongly depends on solvent properties. As Dainton and North (2, 3) have shown, viscosity plays the most important role. The values of k_t (10^6 to 10^8 1/mole s) are additional proof for the termination-step as a diffusion-controlled reaction.

The data on k_p and k_t as reported in the literature differ considerably. Therefore, we conducted new studies on methyl methacrylate (MMA), benzyl methacrylate (BMA), and styrene (St) as monomers. The constants were obtained by applying the method of intermittent illumination (rotating sector) combined with stationary state methods. The viscosity of the solvents varied between 0.5 and 100 cP. No mixed solvents composed of low- and high-molecular components were used but pure solvents only, the molecules of which did not deviate very much from a spherical form (methyl formate, diethyl phthalate, diethyl malonate, dimethyl glycol phthalate, etc.).

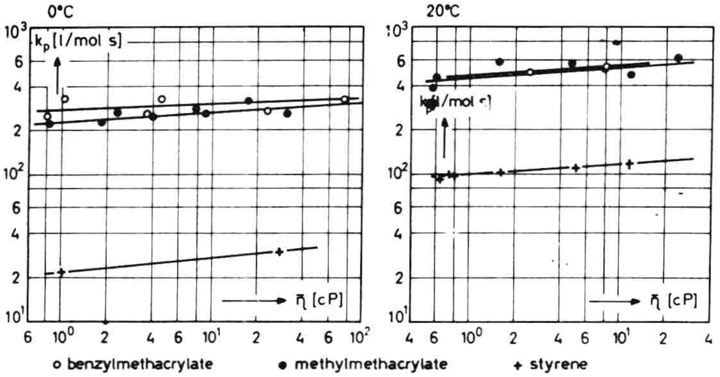

Figure 1. Propagation rate constants of three monomers as a function of solvent viscosity (including the monomer)

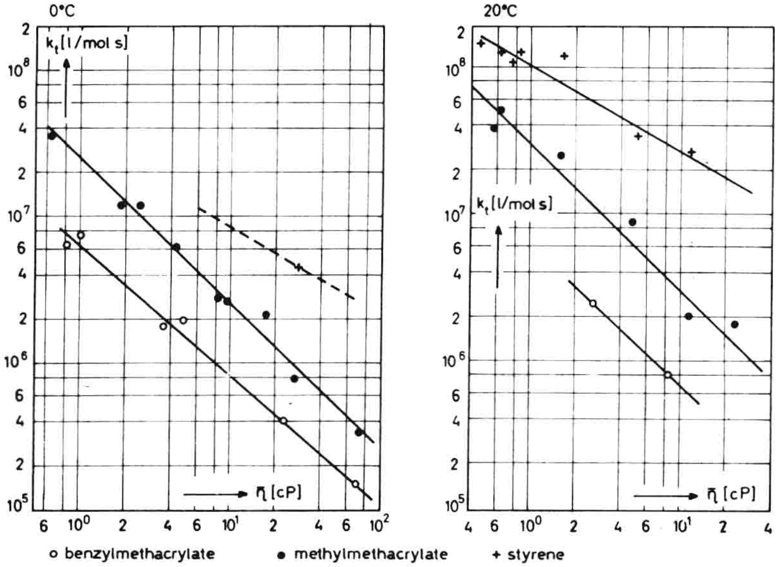

Figure 2. Termination rate constants of three monomers as a function of solvent viscosity

The result is shown in Figures 1 and 2 (*4-7*). In all cases, the propagation constant shows a small increase with increasing viscosity; the increase hardly exceeds the experimental error. We have no definite explanation for this small effect, which has been observed by other authors, too (*8*).

Figure 2 shows the strong dependence of the termination rate constant on the viscosity η of the solvent. For methyl methacrylate, k_t is exactly inversely proportional to η; the two other monomers depend less on η. In any case, this dependence leads to the conclusion that the termination is a diffusion-controlled reaction.

Diffusion of the macroradicals controls can be assumed to be the termination reaction. However, that is not the case; the termination rate constant is absolutely independent of the degree of polymerization, as shown in Table I. Therefore, the assumption must be that the diffusion of the segment at the end of the radical chain controls the termination process (as long as the Trommsdorff effect is not rate-determining).

Table I. Dependence of the Termination Rate Constant on Degree of Polymerization.

$DP \times 10^{-3}$	$k_t \times 10^{-7}$	$DP \times 10^{-3}$	$k_t \times 10^{-7}$
Methyl methacrylate in Diethyl phthalate at 0°C (4)			
3.24	1.03	17.2	0.98
5.50	1.00	23.3	1.01
8.75	0.98	30.0	1.21
11.6	0.98	33.3	1.03
15.0	1.00	62.8	0.98
Styrene in Bis(ethylhexyl phthalate) at 0°C (6)			
0.89	0.46	1.85	0.48
1.39	0.49	3.45	0.42

This assumption has been made by several authors (*2, 3, 8, 10, 11*); but the theoretical models proposed do not sufficiently account for the complete independence of the termination rate constant from the degree of polymerization. Therefore, we have developed a model of the termination process; the model seems to agree better with the experimental results (*12*). We assume that two encountering radical polymer chains partly permeate each other. So an overlapping volume builds up with a certain lifetime. During this overlapping time, the radical end groups can diffuse into that volume and terminate each other by combination or disproportionation (Figure 3).

Use of Smoluchowski's model gives these results:

(1) The diffusion of polymer chain radicals has no influence on the termination rate. This is because the frequency of encounter decreases—by decreasing diffusion constant—to the same extent as the lifetime of the permeation state increases.

(2) The probability of a termination step during an encounter depends on the lifetime and degree of overlapping; on the diffusion constant D_s of the segment of the radical chain end; and on a steric factor α, of the order of 10^{-2}. One obtains: