

BURLANT and HOFFMAN

BLOCK
and GRAFT
POLYMERS

BLOCK and GRAFT POLYMERS

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REINHOLD PUBLISHING CORPORATION

NEW YORK

CHAPMAN & HALL, LTD. LONDON

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Library of Congress Catalog Card Number 60-15996

Photocomposed by THE SCIENCE PRESS, INC., Lancaster, Pa.

Printed in the United States of America

THE GUINN CO., INC.
New York 14, N. Y.

PREFACE

This book summarizes, qualitatively, the reactions and experimental techniques used to initiate block and graft polymerization; it also discusses what is known of the structures of the products and their physical properties. Its purpose is to suggest to scientists and engineers in the plastics field, who are interested in new materials, that "molecular engineering" of polymers—the synthesis of macromolecules of known configuration and physical characteristics—is indeed possible. While at present, the precise relation between structure and properties is unknown for most systems, the utility of this approach is indicated by some briefly studied blocks and grafts, and impressively illustrated by the several polymers for which substantial data are available, namely, the polyoxyalkylene blocks, some rubber grafts, and the polyurethans.

It is a pleasure to thank Dr. Michael Ference, Jr., Executive Director of the Scientific Laboratory of the Ford Motor Company, Dr. J. E. Goldman, Manager of the Physics Department, and Dr. T. W. DeWitt, Manager of the Chemistry Department, for providing the stimulating environment which led to the conception of this book, and the continued encouragement without which it would not have been written.

October, 1960

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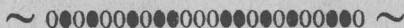
Chapter 1

NOMENCLATURE

A linear *homopolymer* is a chainlike molecule composed of recurring units of a low molecular weight species. Homopolymers may be classified according to the reactions by which they are synthesized: (a) addition polymers, resulting from bond formation by addition of polyfunctional molecules without accompanying byproducts; and (b) condensation polymers, resulting from bond formation between polyfunctional molecules accompanied by elimination of a simple low molecular weight substance, such as H₂O or HCl. Table 1.1 lists common examples in each class.

An *alternating copolymer* is a chain containing two or more different monomer units (indicated by the circles) arranged

(a) in random fashion



(b) in a regularly alternating pattern



or (c) as short sequences



A *graft copolymer* is comprised of a high molecular weight backbone to which a second polymer is attached at intervals along the chain. The backbone may be homopolymeric or copolymeric with pendant groups of either type:

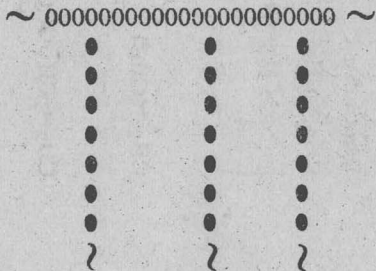


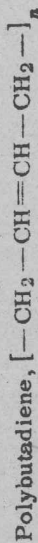
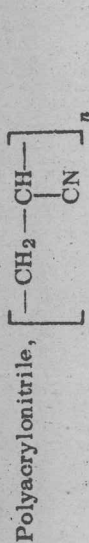
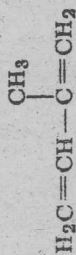
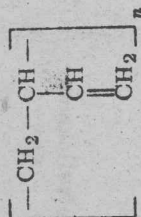


TABLE 1.1. COMMON ADDITION AND CONDENSATION POLYMERS

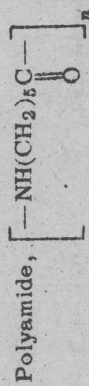
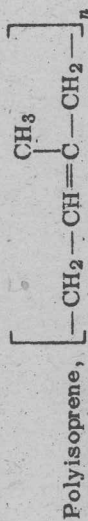
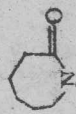
Monomer	Addition	Structure of Polymer
Saturated		
$\text{HO}-\text{R}-\text{OH} + \text{OCN}-\text{R}'-\text{NCO}$	Polyurethan	$\left[-\text{OR}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\text{R}'-\text{NHC}-\overset{\text{O}}{\parallel} \right]_n$
Unsaturated		
$\text{CH}_2=\text{CH}_2$	Polyethylene, $\left[-\text{CH}_2-\text{CH}_2- \right]_n$	
$\text{CH}=\text{CH}_2$ 	Polystyrene, $\left[-\text{CH}-\text{CH}_2- \right]_n$	
$\text{CH}_2=\text{CHCl}$	Polyvinyl chloride, $\left[-\text{CH}_2-\underset{\text{Cl}}{\text{CH}}- \right]_n$	
$\text{CH}_2=\text{CHOOCCCH}_3$	Polyvinyl acetate, $\left[-\text{CH}_2-\underset{\text{OOCCH}_3}{\text{CH}}- \right]_n$	
$\text{CF}_2=\text{CF}_2$	Polytetrafluoroethylene, $\left[-\text{CF}_2-\text{CF}_2- \right]_n$	
$\text{CH}_2=\text{C}-\text{COOR}'$ $\quad \quad \quad $ $\quad \quad \quad \text{R}$	Polyalkyl acrylates, $\left[-\underset{\text{COOR}'}{\overset{\text{R}}{\text{C}}}-\text{CH}_2- \right]_n$	



and

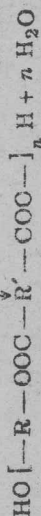
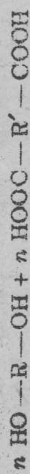


Cyclic



Condensation

Common Method of Preparation



Type

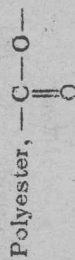
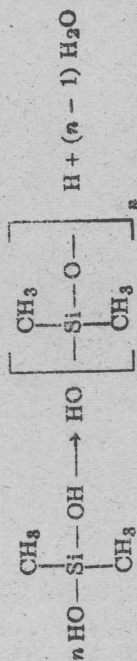
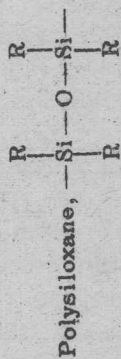
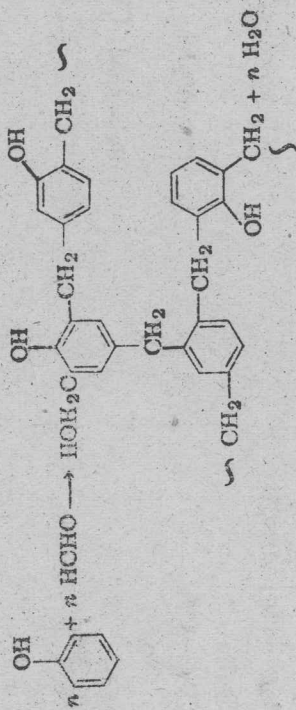
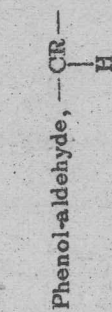
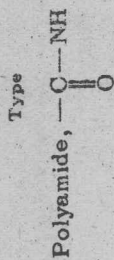


TABLE 1.1. (continued)

Condensation (continued)

Common Method of Preparation



Chapter 2

SEPARATION AND ISOLATION OF BLOCK AND GRAFT POLYMERS

Most of the techniques used to obtain blocks and grafts result in reaction mixtures that contain several polymeric species. Isolation of the pure product is an essential step in the synthesis. Occasionally, it is important to characterize the other polymers which may be present. A problem confronting the chemist, therefore, is the separation and isolation of the components of such a complex polymeric mixture.

From the meager data available in the literature, it appears that the solubility of a block or graft polymer is intermediate between that of the corresponding simple polymers;¹ this property depends mainly on the heat of interaction of the polymer segments with the solvent and is independent of the distribution of the grafted segments on the backbone.^{2,3} The behavior of a rubber-polymethyl methacrylate graft in the presence and absence of precipitants for each component illustrates the effects of these interactions and is described in detail on p. 38.

Because of these solubility characteristics, fractional precipitation, selective extraction, and selective precipitation, using appropriate solvent systems, have been employed successfully to separate the block or graft from the reaction mixture.⁴ The rubber graft described on p. 36, for example, can be isolated from a mixture containing free rubber and polymethyl methacrylate by first extracting the hydrocarbon with a benzene-petroleum ether solution and then titrating a benzene solution of the residue with methyl alcohol. The initial insoluble fraction which appears is the graft, while further addition of alcohol precipitates polymethyl methacrylate.⁵

Using a similar procedure, Woodward and Smets⁶ dissolved a mixture of polystyrene, polymethyl methacrylate, and the corresponding block polymers in chloroform. This solution was fractionated by the addition of methanol. The first few fractions were primarily polystyrene; then block polymer precipitated, and finally, polymethyl methacrylate. The polystyrene content of the block polymer was about 22 per cent.

Almost all the copolymers described in this book have been isolated according to one or more of these procedures.

Turbidimetric titrations of a solution containing blocks, grafts, and homopolymers often furnish useful information about the solubility characteristics of the components and, in some cases, permit the facile isolation of

small quantities of product.^{6,7} The technique depends on the turbidity that results when increasing volumes of a nonsolvent are added to a dilute polymer solution. The shape of the curve obtained when plotting turbidity vs. the volume of precipitant depends on the solubilities of the polymer components in the solution titrated. The titration curve for a mixture of two fractions of a polymer exhibits a well-marked inflection, whereas the curve for a single fraction does not. Similarly, the presence of different chemical species in a polymer mixture, e.g., as in a solution of two homopolymers, is reflected in the slope of the titration curve.

The utility of this technique is indicated by the following example: A mixture containing a polystyrene-polymethyl methacrylate block and the corresponding homopolymers (the preparation of which is described on p. 100) has been characterized by first selectively precipitating the copolymer and polymethyl methacrylate from the mixture with ether (a solvent for the polystyrene employed in these experiments), then turbidimetrically titrating an acetone solution of the block-homopolymer fraction with water as the precipitant.⁸ The curve in Figure 2.1 shows the results of such a

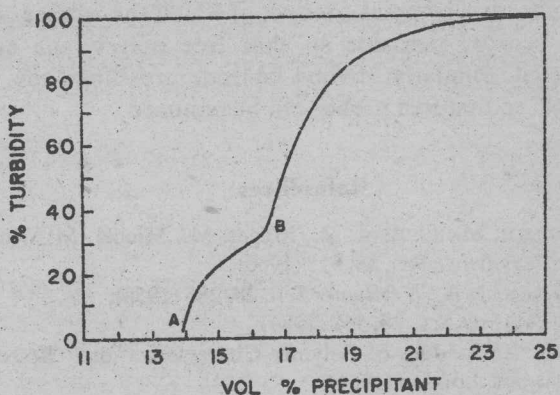


Figure 2.1. Turbidimetric titration curve obtained by aqueous titration of an acetone solution containing polymethyl methacrylate and a polystyrene-polymethyl methacrylate block.⁸

titration. That portion of the curve designated AB represents the contribution to the turbidity of the mixture made by the block component (complete precipitation corresponds to 100 per cent turbidity). Pure block may be isolated from this mixture by several fractionations from acetone with water under controlled conditions: the copolymer so obtained will contain 12 per cent styrene and give a turbidity curve with no point of inflection.

A continuous solvent gradient elution technique has been described for

vinyl acetate grafts to polyvinyl alcohol⁹ as well as for some rubber-methyl methacrylate grafts.¹² In this particularly efficient procedure, the sample mixture is subjected to an increasing concentration of solvent in nonsolvent so that the most soluble component is eluted first and made to travel down a column packed with glass beads. A temperature gradient maintained along the column (highest temperature at the top) results in a sequence of solution-precipitation-solution steps.

Some separation methods depend on the principles of adsorption chromatography. In the case of vinyl acetate grafts to polyvinyl alcohol,⁹ and for a mixed polyamide block system,¹⁰ adsorption on filter paper has proved reliable. Polypropylene stereoblocks can be adsorbed selectively on a substrate of isotactic polymer (p. 156).¹¹

For some select systems, namely block formation to microgels of polystyrene, polyacrylonitrile, and polymethyl acrylate, ultracentrifugation affords a means of separating a block from a mixture of polymers (p. 62).

Occasionally, the unique chemical reactivity of one component in a system can be employed to effect partial separation of a mixture of blocks, grafts, and homopolymers. For example,¹³ mastication of styrene and natural rubber affords a complex product of which the rubber alone can be crosslinked by benzoyl peroxide so that free polystyrene can be conveniently extracted. Similarly, divinyl benzene crosslinks the polystyrene chains exclusively so that free rubber can be removed.

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Chapter 3

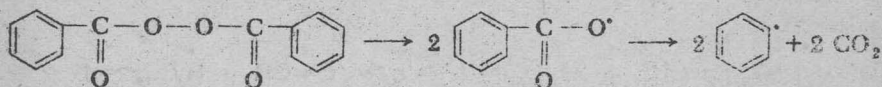
CHAIN TRANSFER REACTIONS

An active site capable of initiating block and graft copolymerization may be formed on a polymer via a "chain transfer" step in vinyl addition polymerizations. While this step may occur both in free radical and ionic systems, only the former has been studied in detail. This chapter begins, therefore, with a review of the mechanisms of those free radical reactions on which chain transfer depends.

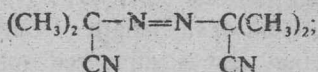
FREE RADICAL POLYMERIZATIONS

HOMOGENEOUS SYSTEMS

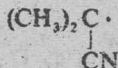
"Chemically" initiated vinyl polymerizations begin with a slow step in which reactive unstable radical species are formed. Benzoyl peroxide, for example, is a good source of radicals. It decomposes at a convenient rate in the neighborhood of 60° as follows:



A particularly useful initiator is α, α' -azobisisobutyronitrile (AZBN),



it decomposes simply to nitrogen and two radicals with the structure

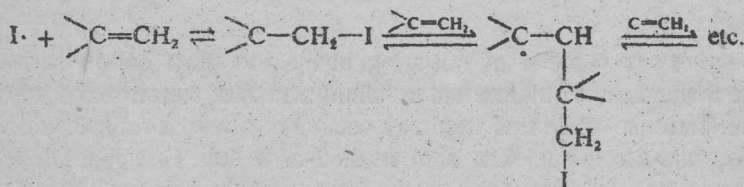


and, unlike the peroxides, is not susceptible to induced decomposition (a result of the reaction between initiator and free radicals present in the system). Organic hydroperoxides (ROOH) also are effective initiators.

The free radicals so formed (I·) initiate polymerization by attacking a monomer molecule thereby creating a new radical species capable of re-

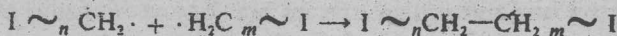
acting in a similar fashion with another monomer molecule; this propagation step is a rapid chain reaction. Note that the initiating fragment is chemically bound to one end of the growing polymer.

Initiation and propagation:

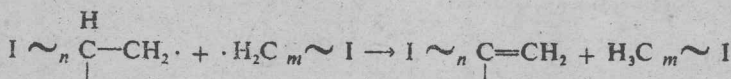


At ordinary temperatures, the chains usually continue to grow until bimolecular termination occurs, either by mutual combination or disproportionation of the macroradicals. For termination by transfer, see p. 11.

Termination by combination:



Termination by disproportionation:



If only the initial stages of the polymerization are considered, it may be assumed that the propagation rate constant, k_p , and the termination rate constant, k_t , are independent of the length of the growing chain, i.e., the reactivity of the "growing" end is influenced only by the last monomer unit. The assumption is also made that a steady state with respect to the formation and destruction of radicals is attained shortly after the reaction begins. The rate equation derived for this radical chain process is therefore

$$\text{Rate} = -\frac{dM}{dt} = k_p \sqrt{\frac{k_i}{k_t}} [M] \sqrt{[I]}$$

where k_p , k_i , k_t are rate constants for propagation, initiation, and termination; $[M]$ and $[I]$ are monomer and initiator concentrations, respectively.

This equation states that the initial liquid phase homogeneous polymerization rate of a vinyl monomer is proportional to the monomer concentra-

tion and to the square root of the initiator concentration. The latter relationship is observed for styrene, vinyl acetate, methyl methacrylate, and a variety of other monomers with and without solvent for a number of initiators. To what extent the rate depends on monomer concentration in solution polymerization, however, is not so clear; in the case of the monomers mentioned, for example, the order is between 1 and 1.5, and depends on the efficiency of the free radicals produced in initiating polymerization.

Gel Effect. At normal temperatures, catalyzed polymerization of some of the common monomers (e.g., methyl methacrylate) is characterized by a marked increase in rate with increasing conversion. The degree of auto-acceleration observed may be reduced by adding a solvent, or increased by adding inert polymer to the system. The phenomenon is particularly noticeable in methyl methacrylate polymerization in solution at conversions exceeding 40 per cent and is accompanied by a simultaneous increase in the molecular weight of the polymer.

This so-called "gel" (or Trommsdorff) effect is explained as follows: bimolecular chain termination of growing radicals in a viscous matrix is controlled by the rate at which these active centers diffuse to each other within the medium. At sufficiently high viscosities, the polymer radicals are not mobile enough to terminate easily in this fashion. On the other hand, chain propagation, initiation, and radical transfer to low molecular weight substances (discussed later) continue normally because the movement of smaller monomer molecules is less affected by changes in the viscosity of the medium.

Chain Transfer. The degree of polymerization (DP : the number of monomer units in a polymer molecule) depends on the ratio of the propagation rate to the termination rate. For the simple vinyl polymerization described above, in which termination by combination occurs,

$$DP = \frac{k_p [M]}{2\sqrt{k_t k_i} \sqrt{[I]}}$$

The average DP for some simple monomers is, in fact, inversely proportional to the square root of the initiator concentration. For many other systems, however, the DP is found to be less than predicted by this simple theory, and the number of polymer molecules produced is greater than the expected value of one or two per pair of initiating radicals (for termination by combination and disproportionation, respectively). Apparently, a reaction occurs in which the free radical site is transferred from the growing polymer chain to some other molecule in the system; chain growth is thus terminated, and the radical formed as a result of the "chain transfer" process may initiate polymerization of a new chain.