nucleus; and indicates that the greatest base strength is found when the amino groups are in the 5,5′-position rather than the 4,4′- and that the non-planar molecule has greater base strength than a corresponding planar molecule.

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Summary

Ultraviolet absorption curves of two dinitrobitolyls and four diaminobitolyls have been determined in alcohol solution. The results give additional information regarding the effect of steric hindrance and position of the substituent group on the absorption of the molecule and are in accord with predicted effects.

The absorption curves of the four diaminobitolyls have been studied in hydrochloric acid solutions of different strengths. Ionization constants for the equilibria between amine, singly and doubly charged ions were calculated by potentiometric and spectrophotometric means.

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Copolymerization. XIV.[1] Copolymerization by Non-radical Mechanisms

BY CHEVES WALLING,* EMORENE R. BRIGGS, WILLIAM CUMMINGS AND FRANK R. MAYO

Although the "copolymerization equation"[2] describing the composition of a copolymer in terms of feed composition and monomer reactivity ratios contains no assumption as to charge type of the active center involved, and although it was noted in the first paper on copolymerization from this laboratory that copolymer compositions may vary with polymerization mechanism,[2b] application of the equation to "ionic" or "polar" polymerizations has only recently been established by Alfrey and Wechsler[3] and by Florin.[4] The purpose of this paper is to report the results of a similar investigation carried out concurrently with early work on radical copolymerization in this laboratory.[2b,5] Because few monomers could be found sufficiently similar in reactivity in ionic polymerization to yield copolymers, the investigation was not carried very far; nevertheless, it showed copolymerization to be an elegant tool for distinguishing between mechanisms of polymerization by different catalysts, and permitted a consideration of some of the differences which distinguish carbonium ion, radical, and carbanion-type polymerizations.

Styrene–methyl methacrylate was the monomer pair chosen for preliminary work. Previous papers have shown that an equimolecular mixture of these substances, polymerized at 60° by a free radical mechanism using benzoyl peroxide as a catalyst, yields an initial copolymer containing 51 mole % styrene, and this composition is unchanged by the addition of good or poor solvents[2b,6,7] or by carrying out the reaction in emulsion,[8] and is only slightly affected by changes in temperature.[7] Strikingly different results are obtained when these monomers are copolymerized using "ionic" catalysts. On the one hand, stannic chloride or boron trifluoride etherate leads to an initial polymer consisting of almost pure polystyrene. On the other, metallic sodium or potassium produces initially over 99% pure polymethyl methacrylate (*cf.* Table I).

Stannic chloride and boron trifluoride etherate belong to the class of generalized acid or Friedel–Crafts-type catalysts which apparently, providing a proton source[9,10] or other suitable material[11] is available, give rise to polymerization through an active center of the carbonium ion type.[12,13] The composition of the styrene–methyl methacrylate product, in keeping with both the failure of acid catalysts to polymerize methyl methacrylate alone and the ready solvolysis of compounds such as the α-phenethyl halides,[14] supports the idea that a substituted benzyl carbonium ion is more stable and more easily formed than a carbonium ion with an α-carbomethoxy group.

The result with metallic sodium or potassium is even more interesting, since it helps to establish the mechanism of this type of polymerization, for which both radical[15] and carbanion[16] active cen-

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* Harvard College B.A. 1937.

(1) For the preceding paper in this series, see Walling, THIS JOURNAL, **71**, 1930 (1949).

(2) (a) Alfrey and Goldfinger, *J. Chem. Phys.*, **12**, 205 (1944); (b) Mayo and Lewis, THIS JOURNAL, **66**, 1594 (1944); (c) Wall, *ibid.*, **66**, 2050 (1944).

(3) Alfrey and Wechsler, *ibid.*, **70**, 4266 (1948).

(4) Florin, *ibid.*, **71**, 1867 (1949).

(5) Lewis, Mayo and Hulse, *ibid.*, **67**, 1701 (1945).

(6) Nozaki, *J. Polymer Sci.*, **1**, 445 (1946).

(7) Lewis, Walling, Cummings, Briggs and Mayo, THIS JOURNAL, **70**, 1519 (1948).

(8) Smith, *ibid.*, **68**, 2067 (1946).

(9) Evans, Holden, Plesch, Polanyi, Skinner and Weinberger, *Nature*, **157**, 102 (1946).

(10) Norrish and Russell, *ibid.*, **160**, 543 (1947).

(11) Pepper, *Trans. Faraday Soc.*, **45**, 397 (1949).

(12) Whitmore, *Ind. Eng. Chem.*, **26**, 94 (1934).

(13) Williams, *J. Chem. Soc.*, 775 (1940).

(14) Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, 1940, Ch. V and VI.

(15) Bolland, *Proc. Roy. Soc.* (*London*), **A178**, 24 (1941).

(16) (a) Price, "Reactions at Carbon–Carbon Double Bonds,"

ters have been proposed. Since the copolymer is different from that obtained in known free-radical polymerizations, at least this particular copolymer must be formed by a carbanion mechanism,[17] and a similar inference may be drawn for the case of styrene–butadiene where the sodium-catalyzed copolymerization of a 1:3 feed yields an initial product containing 30% styrene, compared with 19% for the radical reaction.[18]

Further, although both styrene and methyl methacrylate may be polymerized by sodium, it is noteworthy that the preferred addition of a carbanion is to form the more stable and less basic enolate ion from methacrylate rather than the substituted benzyl carbanion from styrene.

The result of the sodium and potassium-catalyzed experiments also indicates that the mechanism for the acid-catalyzed polymerization of isobutylene involving chain growth by both carbonium ion and carbanion centers proposed by Norrish and Russell[10] cannot be a general one for acid-catalyzed polymerizations, since, if it were, the product of the stannic chloride catalyzed experiment would have to contain appreciable quantities of methacrylate.

Mechanistically, if schemes involving "energy chains" or undefined "activated double bonds" are excluded, chain growth through active centers involving free radicals, carbonium ions and carbanions seemingly exhausts the possibilities for vinyl polymerization. Since the copolymerization of styrene and methyl methacrylate by these three mechanisms yields sharply differing products, use of this pair should provide a useful means of determining the mechanism of action of new polymerization catalysts. This method has already been used to establish the identity of the active center in the benzoyl peroxide-catalyzed and thermal reactions in the first paper of this series.[2b] Some further illustrations are given in Table I. Polymerizations in the presence of ultraviolet light, magnesium perchlorate, and thymol yield copolymers containing approximately equal quantities of the two monomers and clearly indicate a free radical reaction. The light-catalyzed polymerization was carried out because early workers had suggested an "activated double bond" mechanism for photopolymerization,[19] although the free radical mechanism is now generally accepted. The magnesium perchlorate experiment was made because it had been observed that monomers dried over magnesium perchlorate frequently polymerize,[20] and this reagent is both an oxidizing agent and a (rather weak) generalized acid. The thymol experiments were carried out because the polymerization of styrene in that solvent has been interpreted both as a carbonium ion reaction[21] and

TABLE I

MOLE % STYRENE IN INITIAL POLYMER FORMED FROM 1:1 STYRENE–METHYL METHACRYLATE MIXTURES USING VARIOUS CATALYSTS

Catalyst	Temp., °C.	% Styrene in initial polymer
Bz_2O_2	60	51[2b]
None	60	51[2b]
None	131	51
$SnCl_4$	30	>99
BF_3 etherate	30	>99
Na	30	<1
K	30	<1
Light	60	51
Thymol	131	49.5
$MgClO_4$	30	50

TABLE II

EFFECT OF CATALYST ON INITIAL COPOLYMER COMPOSITIONS FOR SEVERAL MONOMER PAIRS

Catalyst	Temp., °C.	Mole % first monomer in initial polymer
	Styrene–Acrylonitrile	
$SnCl_4$	30	>99
Bz_2O_2	60	58[5]
	Styrene–Vinylidene Chloride	
$SnCl_4$	30	>99
Bz_2O_2	60	72[5]
	Styrene–*p*-Methoxystyrene	
$FeCl_3$	30	< 1
Bz_2O_2	60	54[a]
	Styrene–Vinyl Acetate	
$SnCl_4$	30	>90
Bz_2O_2	60	98.3[b]
	Styrene–Diethyl Fumarate	
$SnCl_4$	30	>96
Bz_2O_2	60	55[7]
Na	30	No polymer
	Styrene–Vinyl Ethyl Ether	
$FeCl_3$	30	< 9
Bz_2O_2	60	>99[23]
	Methyl Methacrylate–Acrylonitrile	
$SnCl_4$	30	No polymer
Bz_2O_2	60	69[5]
Na	30	<10
	Vinyl Acetate–Vinyl Ethyl Ether	
$FeCl_3$	30	< 4
Bz_2O_2	60	80

[a] Walling, Briggs, Wolfstirn and Mayo, *ibid.*, **70**, 1537 (1948). [b] Mayo, Walling, Lewis and Hulse, *ibid.*, **70**, 1523 (1948).

Interscience Publishers, Inc., New York, N. Y., 1946, p. 117; (b) Beaman, THIS JOURNAL, **70**, 3115 (1948); (c) Robertson and Marion, *Can. J. Research*, **26B**, 657 (1948).

(17) This result gives no indication whether addition is a rapid chain reaction, or involves slow stepwise addition to relatively stable sodium-growing polymer ion pairs. It does mean, however, that any growing sodium–polymer complex reacts ionically, rather than by splitting into radicals.

(18) Schulze and Crouch, THIS JOURNAL, **70**, 3891 (1948).

(19) Melville, *Proc. Roy. Soc.* (*London*), **A163**, 511 (1937); *cf.* Waters, "The Chemistry of Free Radicals," the Clarendon Press, Oxford, 1946, p. 194.

(20) *Cf.* Lilley and Foster, *Nature*, **160**, 131 (1947).

(21) Moore, Burk and Lankelma, THIS JOURNAL, **63**, 2954 (1941).

as a thermal (free radical) reaction somewhat inhibited by thymol.[22] The copolymerization results strongly support the latter alternative.

Other Monomer Pairs.—The effects of change of catalyst on copolymer compositions for some other monomer pairs are listed in Table II, and clearly show the change in copolymer composition which usually accompanies a change in reaction mechanism. The results on styrene–vinylidene chloride and styrene–vinyl ethyl ether confirm those of Florin,[4] and the data in general also illustrate what appears to be rather a general principle of ionic polymerizations: changes in structure usually produce much greater changes in reactivity than in the radical reaction, with the result that the formation of a copolymer containing appreciable quantities of both components is infrequent. In none of our work has a phenomenon been observed analogous to the "alternating effect" arising in radical copolymerizations[2b,23] (which permits the inclusion in a copolymer of a monomer apparently incapable of polymerizing alone).[24] Although the data of Tables I and II do not permit lengthy discussion of the effects of structure on reactivity in ionic polymerizations, a few comments seem worthwhile and are given in the next two sections.

Reactivities in carbonium ion polymerizations may be estimated partly from copolymerization experiments and partly from measurements of catalyst strengths necessary to induce polymerization.[25] They lie in the order vinyl ethers > dienes > styrene and isobutylene. The results of Alfrey and Wechsler[3] and Florin[4] indicate that halogen substituents in general deactivate the double bond. In our experience and in contrast to an early report to the contrary,[26] vinyl acetate, vinyl halides, and carbonyl-conjugated olefins do not yield high polymers by a carbonium ion mechanism, even in the presence of as strong catalysts as stannic chloride. The observed order seems in good agreement with the idea that reactivity of an olefin in carbonium ion polymerization is determined primarily by electron availability at the double bond and by the degree of resonance stabilization of the resulting carbonium ion. It thus roughly parallels the polarity series observed in radical copolymerizations.[23]

Carbanionic polymerizations appear much the most limited in scope of the three types, largely because of other competing reactions of many monomers with a catalyst such as sodium. The order of reactivity seems to be nitrile-conjugated olefins > carbonyl-conjugated olefins > dienes and styrene, paralleling the ease of addition of other negative ions, and is probably accounted for by the resonance stabilization (inverse of the base-strength) of the resulting carbanions.

Experimental

Materials.—Monomers were the same as employed in previous papers in this series, usually commercial materials fractionated before use. For use in the alkali-metal-catalyzed reactions they were stored over Drierite while for carbonium ion polymerization it was found advantageous to add a trace of inhibitor, hydroquinone or *t*-butylcatechol, to suppress any free-radical reaction.

Copolymerizations by radical mechanism were carried out in sealed evacuated tubes as described in previous papers in this series.[2b] For the light-catalyzed reaction, Corex D glass reaction tubes were used, illuminated at a distance of 7.5 cm. by a Hanovia Type A mercury arc with a quartz jacket and no filter. Alkali-metal-catalyzed reactions were carried out similarly except that the monomers were diluted with benzene (1:1) to decrease viscosity and the reaction tubes shaken by a shaking machine during polymerization. The catalyst was added as a freshly cut piece of metal before evacuation, or else the monomers were distilled on the vacuum line into the reaction tube, the walls of which had been coated with a sodium mirror. The two methods gave identical results. Most of the acid-catalyzed polymerizations were simply carried out in air in test-tubes which were stoppered after addition of the catalyst. Under these conditions the reaction had an induction period of several minutes, but re-

TABLE III

EXPERIMENTAL DATA ON COPOLYMERIZATIONS BY DIFFERENT CATALYSTS

Catalyst	Temp. °C.	Time, hr.	$[M_1]_0$[a]	$[M_2]_0$[a]	$[M_1]$[a]	$[M_2]$[a]	C, %
			Styrene (M_1)-Methyl Methacrylate (M_2)				
$SnCl_4$[b]	30	3	43.5	46.9	21.8	46.9	92.20
BF_3 eth.[c]	30	48	43.5	46.9	2.6	46.9	91.50
Na[d]	30	20	43.5	46.9	43.5	42.2	60.30
K[d]	30	48	43.5	46.9	43.5	12.3	59.80
Light	60	24	20.88	47.82	13.80	34.49	71.51
Light	60	24	48.23	12.36	42.39	10.17	83.70
$Mg(ClO_4)_2$[d]	30	48	48.6	51.3	47.8	50.5	76.1
Thymol[e]	131	24	40.87	39.55	23.13	21.68	76.40
Thymol[e]	131	24	41.08	40.61	23.80	23.20	76.45
			Styrene (M_1)-Acrylonitrile (M_2)				N, %
$SnCl_4$[b]	30	0.5	100	100	60	...	0.26
			Styrene (M_1)-Vinylidene Chloride (M_2)				Cl, %
$SnCl_4$[b]	30	0.5	41.1	41.3	2.6	...	0.37
			Styrene (M_1)-*p*-Methoxystyrene (M_2)				C, %
$FeCl_3$[f]	30	0.5	75.0	25.0	...	20.1	80.7

[a] Unreacted monomers in millimoles at start (subscript zero) and end of reaction. [b] Approx. 0.2 cc. [c] 5 drops of commercial BF_3 etherate. [d] Approx. 100 mg. [e] One mole per mole total monomers. [f] 0.05 ml. of 5% $FeCl_3$ in ethyl acetate.

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[22] Walling, THIS JOURNAL, **66**, 1602 (1944).

[23] Mayo, Lewis and Walling, *ibid.*, **70**, 1529 (1948).

[24] Thus, in contrast to the numerous commercial copolymers prepared by free-radical copolymerization, the only ionic copolymer in large-scale technical use is butyl rubber, prepared by the low-temperature "carbonium ion" copolymerization of isobutylene and a conjugated diene.

[25] Unpublished experiments: vinyl ethers are violently polymerized by such weak catalysts as traces of iodine; dienes require ferric chloride in esters or dioxane; styrene, in turn is polymerized rapidly by ferric chloride only in non-basic solvents such as chloroform.

[26] Marvel and Riddle, THIS JOURNAL, **62**, 2666 (1940).

sults were the same as in experiments in which catalyst was distilled into monomer on a vacuum line and the reaction tubes then sealed in absence of air.

Polymers were worked up and analyzed as described in previous papers, and results of sample experiments are listed in Table III. Results on a number of systems summarized in Table II are omitted since single experiments at 1:1 feed only were carried out. Further, some of these yielded dark, sticky, or insoluble polymers which may have retained some monomer during purification. Accordingly, here only an upper limit to the amount of the least reactive monomer in the polymer is indicated. For the styrene–methacrylate systems catalyzed by light or magnesium perchlorate or carried out in thymol, monomer reactivity ratios were determined graphically in the usual way[2b] and used to calculate the compositions in Table I. For the remainder of the examples given, the analytical results illustrate that no copolymer was formed.

Summary

1. The initial copolymer formed from 1:1 styrene–methyl methacrylate mixtures is shown to be essentially pure polystyrene for the stannic chloride or boron trifluoride-catalyzed reaction and essentially pure polymethyl methacrylate for the reaction in the presence of sodium or potassium.

2. The results are considered as evidence for carbonium ion and carbanion mechanisms respectively for polymerizations in the presence of these two classes of catalysts, and it is suggested that copolymerization studies should provide a sensitive tool for establishing the mechanism of polymerization in the presence of other catalysts.

3. Data are presented on copolymer compositions obtained in the non-radical copolymerizations of some other monomer pairs, and the effects of structure on reactivity in ionic polymerizations are discussed.

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[CONTRIBUTION FROM THE WHITMORE LABORATORY OF THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

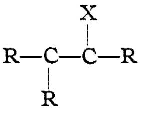
Hydrocarbons. X.[1] Three New Octenes

BY F. C. WHITMORE,[2] H. E. WHITMORE[3] AND N. C. COOK

Introduction

Of the 66 possible structural isomers of the octenes, excluding *cis* and *trans* forms, 63 have been reported. This paper reports the syntheses of the three remaining octenes: 5,5-dimethyl-2-hexene, 2,4-dimethyl-3-hexene and 3-ethyl-4-methyl-1-pentene.

The dimethylhexenes were made as part of a program involving a spectrometric study of olefin types. These olefins were prepared by dehydration of the appropriate alcohols, which were readily synthesized through the Grignard reaction. Separation of the olefins, especially the geometric isomers, required columns of more than 200 theoretical plates.

3-Ethyl-4-methyl-1-pentene was made primarily to complete the octene series. The difficulty of making halides of the type[4]  $\mathrm{R{-}\overset{X}{\overset{|}{C}}{-}\underset{R}{\underset{|}{C}}{-}R}$ ruled out the probability of making the compound through such a Grignard reagent. After several unsuccessful attempts, a method was developed which involved the acetylation of 2-methyl-2-pentene to give 3-ethyl-4-methyl-4-pentene-2-one. Complete hydrogenation of this ketone, followed by dehydration of the alcohol, gave a 30% yield of 3-ethyl-4-methyl-1-pentene, accompanied by other isomers which were easily separated.

Although all the octene isomers have now been reported, a considerable number should be resynthesized, particularly those having geometric forms. The early investigators were unable to prepare in high purity many of the close boiling isomers because of the lack of precision fractionating equipment. Some work of this nature is in progress in this Laboratory and will be reported in subsequent papers.

Experimental

5,5-Dimethyl-2-hexene.—Ethylene was alkylated with *t*-butyl chloride in the presence of aluminum chloride[5] to give a 65% yield of 3,3-dimethyl-1-chlorobutane.

3,3-Dimethylbutylmagnesium chloride was prepared in 90% yield (20 moles) in a water-jacketed copper Grignard reactor (20-liter capacity), equipped with a motor driven stirrer, dropping funnel and condenser. From the reaction of 867 g. of redistilled acetaldehyde with the Grignard reagent was obtained a 60% yield of fractionated 5,5-dimethyl-2-hexanol, b. p. 166°, n^{20}_D 1.4229.

The above alcohol was dehydrated at 360° over Grade F-1, Mesh 4-8 activated alumina (Alorco) at a feed rate of 600 ml. per hour. Fractionation of 1840 g. of the dehydration product through a column of more than 200 theoretical plates,[6] gave 218 g. (cuts 4–12) of 5,5-dimethyl-1-hexene (I), b. p. 103°, n^{20}_D 1.4040; the 416 g. of intermediate fractions; 40 g. (cuts 38–41) of a low boiling form of 5,5-dimethyl-2-hexene (II), b. p. 104°, n^{20}_D 1.4051; 72 g. of intermediate fractions; and 560 g. (cuts 49–59) of

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(1) For paper IX see, Moersch and Whitmore, THIS JOURNAL, 71, 819 (1949).

(2) Deceased; Harvard University Ph.D. 1914.

(3) Present address: Universal Oil Products Co., Chicago, Illinois.

(4) Whitmore and Johnston, THIS JOURNAL, 55, 5020 (1933).

(5) Schmerling, *ibid.*, 67, 1778 (1945).

(6) Column description: 300 cm. × 1.5 cm., packed with 1/16" stainless steel helices, single turn.