Block Copolymerization of Formaldehyde

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Synopsis

Solubility and spectroscopic evidence are presented to support the formation of A–B block copolymers between monomers undergoing anionic polymerization (A units) and monomeric formaldehyde (B units). Comonomers included in the study were styrene, methyl and n-butyl methacrylate, acrylonitrile, isoprene, and N,N-di-n-butylacrylamide. Similar evidence is presented on the formation of B–A–B copolymers between styrene and α-methylstyrene and formaldehyde; an A–(B–C) random copolymer of styrene, formaldehyde, and phenyl isocyanate (C) was also prepared. Experimental details for the preparation of high-purity, monomeric formaldehyde suitable for such work is described in some detail. It should be emphasized that this study was directed primarily toward showing the feasibility of preparing formaldehyde block copolymers; therefore, further work is needed to establish the quantitative nature of these reactions.

INTRODUCTION

Monomeric formaldehyde can be polymerized by using either anionic or cationic initiators.[1] Thus, it seems reasonable that "living" polyanions[2,3] can be used to prepare block copolymers of formaldehyde. This idea has been pursued by several groups of workers and has subsequently formed the foundation for several patents[4-7] and at least two scientific publications.[8,9] It is pertinent to note that one of these publications[8] reported on the successful preparation of block copolymers of styrene and formaldehyde while the other reported[9] that formaldehyde reacted with the original polystyryl anions to give only formate endgroups. The present paper presents data which corroborate the position that such block copolymers can indeed be formed and demonstrates the wide applicability of the basic concept. Since the authors believe that one of the primary reasons for the disagreement between results of previous workers could well be differences in formaldehyde purity, a rather complete description of the procedure we used to prepare monomeric formaldehyde is included.

Basically, the block copolymers which were prepared were of three different types: (*1*) those containing a single block of A units followed by a sequence of B units (formaldehyde); (*2*) those containing a sequence of A units and having a sequence of B units on each end of the polymer chain; and (*3*) those containing a squence of A units and a block of (B–C) units, where C represents a third monomer which is copolymerized with the for-

maldehyde in a random fashion. In the A–B copolymers, the A units were styrene, methyl methacrylate, n-butyl methacrylate, acrylonitrile, iso-prene, and N,N-di-n-butylacrylamide. B–A–B copolymers containing styrene and α-methylstyrene and one A–(B–C) copolymer containing styrene and phenyl isocyanate were also studied.

Much of this work was patterned after the work on the styrene–formaldehyde system. Thus, the preparation, characterization, and physical properties of this particular copolymer will be covered in greatest detail. Some of the other copolymers were only studied sufficiently to show that block copolymers were formed.

EXPERIMENTAL

Formaldehyde Monomer

The preparation of high-purity monomeric formaldehyde presents many problems. Not only does the monomer undergo both acid- and base-catalyzed side reactions, but it also has a strong tendency to polymerize. The polymerization can be initiated by at least two of the impurities which are almost always present in an impure formaldehyde stream, i.e., water and methanol. Thus, it is not surprising that a delicate "balance" of conditions is necessary in order to obtain high-purity monomer suitable for the preparation of block copolymers.

Impure monomeric formaldehyde was generated from either paraformaldehyde or α-polyoxymethylene by thermal decomposition. The gaseous
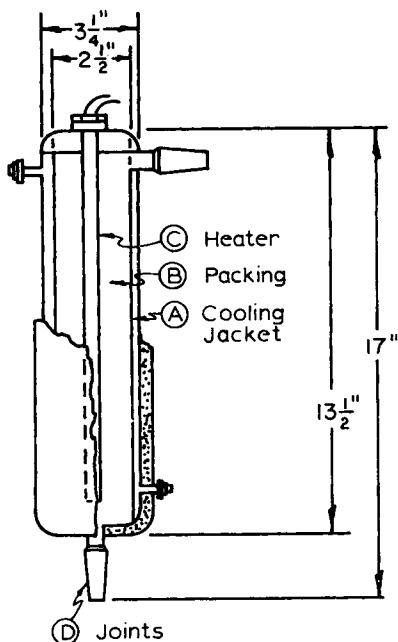

Fig. 1. Formaldehyde purification column

TABLE I
Influence of L/D on Formaldehyde Purity at $-78°C$. Column Temperature

L/D	Gas rate, cc./min.	Analyses			
		Form- aldehyde, wt.-%	Water, wt.-%	Methanol, wt.-%	Methyl formate, wt.-%
3.3	1820	99.97	0.00	0.00	0.03
6.6	2500	99.91	0.02	0.00	0.07
13.3	2500	99.88	0.04	0.05	0.03

TABLE II
Effect of Column Temperature on
Formaldehyde Production and Purity at an L/D Ratio of 6.6

Temperature, °C.	Relative amount of formaldehyde	Analyses			
		Form- aldehyde, wt.-%	Water, wt.-%	Methanol, wt.-%	Methyl formate, wt.-%
−78	1	99.91	0.02	0.03	0.03
−56	10.5	99.83	0.01	0.04	0.12
−47	12.7	99.86	0.01	0.02	0.11
−42	—	99.85	0.03	0.02	0.10

decomposition products were then carried through a cold, packed column using argon as a carrier gas. A schematic drawing of the column is shown in Figure 1. Early work showed that glass columns were frequently broken by the formation of polymer on the glass surface; hence, a stainless steel column was used throughout most of the work. The column consisted of a cooling jacket (A) for the circulation of cold acetone; packing (B) for improved separation efficiency (0.24 × 0.24 in. protruded nickel packing from Penn State College was found to be most effective); and a heater (C) through the center of the column for *in situ* regeneration. The joints (D) were $^{35}/_{45}$ in size. In a typical run, the predried column was mounted on the top of a three-necked flask and cooled to the desired temperature under a stream of argon. α-Polyoxymethylene was added to the preheated flask. Argon was passed through the flask, then through the column to carry the decomposition products to the reactor. The column became fouled with solid polymer after several hours operation and had to be regenerated by heating under a strong current of argon.

Several experiments were made to determine the effect of column geometry on formaldehyde purity. The influence of length/diameter (L/D) ratio for a column packed with protruded nickel packing at essentially a constant rate of argon flow is shown by the data in Table I. These data were taken at a column temperature of $-78°C$. Analyses were made by gas–liquid chromatography according to the method of Bombaugh and Bull.[10] Note that an L/D of only 3.3 was sufficient to purify the formaldehyde stream to approximately the 99.9% level. The last traces of im-

purities could not be removed by simply increasing the amount of packing in the column.

The influence of column temperature on formaldehyde purity was also studied. Data which were obtained at an L/D ratio of 6.6:1.0 are summarized in Table II.

Although the methyl formate content of the formaldehyde stream increased between the temperatures of -78 and $-48°C.$, the water and methanol contents remained essentially constant. In two instances, the water level was below 100 ppm. With extreme care in monomer handling and sampling this level of monomer purity or a higher one was achieved routinely by this purification procedure. Because the amount of formaldehyde in the effluent stream increases as column temperature increases and because methyl formate has a low chain-transfer activity,[11] most of the monomeric formaldehyde was purified at $-45°C.$

Monomers

Monomers were purified just prior to use and handled under dry, oxygen-free argon. Styrene monomer (Dow Chemical Company) was passed through calcined alumina and distilled *in vacuo*. This same procedure was used to purify quantities of methyl methacrylate and *n*-butyl methacrylate (Rohm & Haas Company). Acrylonitrile (Matheson, Coleman and Bell) was dried over molecular sieves and distilled at atmospheric pressure. Polymerization-grade isoprene (Phillips Petroleum Company) was distilled from *n*-butyllithium. About one-half of the isoprene polymerized during distillation, but the distillate was free of polymer. α-Methylstyrene (Matheson, Coleman and Bell) was distilled from sodium hydride *in vacuo*. Phenyl isocyanate (Matheson, Coleman and Bell) was distilled at 48°C. at 10 mm. Hg. Argon (Chemical Division, Gulf Oil Corporation) exhibited less than 8 ppm total impurities.

Solvents

Solvents were purified immediately prior to use and kept under a blanket of dry, oxygen-free argon. Tetrahydrofuran (Matheson, Coleman and Bell), toluene, and xylene (Mallinckrodt Chemical Company) were all purified by distillation from either sodium or calcium hydride. Thiophene-free benzene (Mallinckrodt Chemical Company) was distilled from *n*-butyllithium. Diethyl ether (Mallinckrodt Chemical Company) was passed through a column of calcined alumina to remove peroxides. *N,N*-Dimethylformamide (Matheson, Coleman and Bell) was distilled to obtain a fraction boiling at 150–151°C.

Initiators

Sodium naphthalenide, *n*-butyllithium, and 9-fluorenyllithium were used as anionic initiators. The *n*-butyllithium was used in heptane solution as supplied by Foote Mineral Company. 9-Fluorenyllithium was prepared as a 0.25N solution in ethyl ether by the method of Glusker et al.[12,13]

Sodium naphthalenide was prepared by adding 1.28 g. of dry naphthalene and 0.5 g. of freshly pressed sodium ribbon to 100 ml. of purified tetrahydrofuran under an inert atmosphere. The sodium naphthalenide formed almost immediately to give a green color which became intense after several minutes. A $0.1N$ solution could be stored at least 7 days if moisture and oxygen were carefully excluded.

Flow Diagram and Material Balance

A flow diagram showing the formaldehyde purification system and the polymerization reactor is given in Figure 2. The formaldehyde from the generator (C) was passed into the purification column, the operation of which has already been described. The formaldehyde–argon stream from the purification column was led to the reactor (B) through polyethylene tubing. This line was kept as short as possible in order to mininize plugging due to polymer formation. The highest utilization of formaldehyde monomer was obtained by bubbling the formaldehyde–argon stream through the reaction medium in the reactor (B). However, by operating this way, the monomer-inlet tube sometimes became plugged with polymer and had to be cleaned through the use of a metal probe. The effluent gas was passed through two bubblers (D) containing dry mineral oil. Figure 2

	Wt. %
HCHO	99.86
H₂O	0.007
MeOH	0.018
HCOOMe	0.116
	100.001

Recovery = 93.1 %

	Wt. %
HCHO	99.14
H₂O	0.48
MeOH	0.32
HCOOMe	0.06
	100.00

(A) Purification Column

Coolant

Thermocouple

Argon

Recovery 22.8%
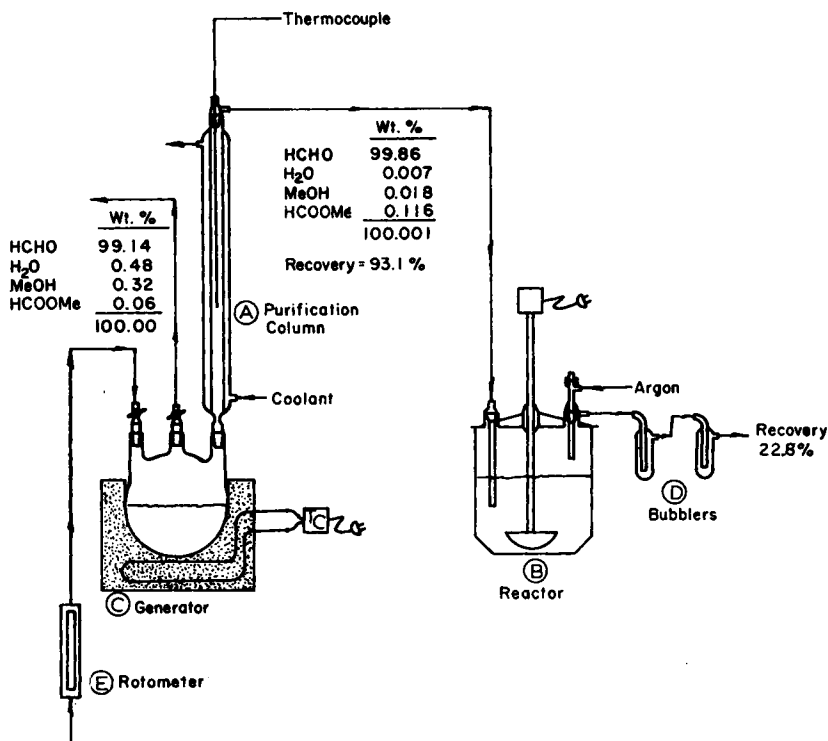
(D) Bubblers

(B) Reactor

(C) Generator

(E) Rotometer

Fig. 2. Flow diagram.

also shows formaldehyde analyses and monomer recovery values for a typical run. Thus, it is seen that 93% of the formaldehyde monomer which left the generator (C) was available for reaction; the remainder was retained in the purification column (A). Of the formaldehyde available for reaction, about 23% was found in the effluent stream from the bubblers (D). These numbers indicate that approximately 70% of the formaldehyde generated at (C) ended up as product in the reactor (B). Although this value varied, it usually ranged between 50 and 75%.

Capping Procedure

The formaldehyde copolymers, as prepared, had hydroxyl groups on at least one end of the polymer chain. Such polymers undergo a thermal unzipping of the chain to yield monomeric formaldehyde.[14] It is known that this thermal instability can be overcome to a great extent by "capping" the terminal hydroxyl groups with acetate endgroups.[15] Therefore, in order to minimize the influence of decomposition, all of the copolymers were acetylated prior to making any physical measurements. Typically, the acetylation procedure involved charging about 110 g. of copolymer, 5 g. of sodium acetate, 3500 ml. of xylene, and 200 ml. of acetic anhydride to a stirred, three-necked flask equipped with a reflux condenser. While purging with argon, the reaction mixture was heated to 120°C. and held at that temperature for about 4 hr. The reaction slurry was cooled to room temperature and washed in a Waring Blendor several times with xylene and then in a similar fashion with methanol. Approximately ten volumes of solvent per gram of polymer was used. The final product was dried at 50–60°C. *in vacuo*. Yields were usually around 95%. The rate of thermal decomposition of the copolymers at this point, as measured by the so-called "syringe" stability test developed by DuPont,[15] was about 0.3%/min. at 222°C. Some of the samples were stabilized further by blending with a combination of an antioxidant and a thermal stabilizer by using a Brabender Plasti-Corder. The blending was done at 190°C. for a period of 10 min. Polymers which contained stabilizers usually had decomposition rates of 0.05–0.08%/min. at 222°C.

Solution Viscosities

Inherent viscosities were measured at 150°C. in N,N-dimethylformamide at a polymer concentration of 0.5 g./dl.; 0.1% diphenylamine was added as an antioxidant.

FORMALDEHYDE HOMOPOLYMERIZATION

The length of the formaldehyde sequences (B) which become attached to the other sequences (A) in block copolymers is dependent upon the amount of chain transfer which occurs during the formaldehyde polymerization step. Therefore, an experiment was run in order to determine the "living" nature of the homopolymerization of formaldehyde in n-heptane

at room temperature with n-butyllithium as the initiator. The findings definitely support the fact that the molecular weight of the product increases with reaction time. Thus, after 2.0 and 4.0 hr. reaction time, inherent viscosities of the products were 0.70 and 1.26 dl./g., respectively. These data suggest that, under "vacuum line" conditions, high-purity, monomeric formaldehyde might undergo "living" polymerization. These data also attest to the purity of the formaldehyde used in this work which, among other factors, is of great importance in obtaining block copolymers.

A–B COPOLYMERS CONTAINING STYRENE

Work on styrene–formaldehyde copolymers served as a model for work on other polymers. After many experimental trials, the procedure which was found to give the highest yield of styrene–formaldehyde block copolymer was as follows.

Approximately 50 cc. of purified benzene was added to a 2-liter resin flask which had been previously dried in an oven at 120–140°C. and purged with high-purity argon. Purified styrene and the desired amount of n-butyllithium were added through use of hypodermic syringes. By adding the initiator slowly, it was possible to get a qualitative measure of the purity of the system. Thus, with highly purified reagents, less than 0.1 mmole of n-butyllithium was necessary in order to obtain a yellow-colored solution and to initiate polymerization. Higher concentrations of initiator turned the polymerization mixture to a persistent orange color. After about 1 hr. at 25–30°C., the conversion of monomer to polymer was usually between 80 and 90%. At this point, the reaction temperature was lowered to about 10°C. and a flow of purified formaldehyde monomer was started through the reactor. As the formaldehyde reacted with the polystyryl anion, the yellow-orange color disappeared. This change was rapid and usually took less than 30 sec. The remainder of the benzene, 950 cc., was added to the reaction flask and formaldehyde addition was continued for the desired period of time. A postpolymerization period of about 30 min. was allowed for the formaldehyde dissolved in the reaction medium to polymerize after the flow of formaldehyde monomer was stopped. Methanol was used to terminate the reaction. The product was separated by filtration and dried in a vacuum oven at 50°C.

Proof of Structure

Experiments were run to try to separate the two possible homopolymers A and B through selective extraction of homopolymer A. The general procedure is illustrated by the following work on styrene–formaldehyde copolymers. A styrene–formaldehyde copolymer was washed several times with toluene in a Waring Blendor and filtered after each washing. This material was extracted for 24 hr. with boiling toluene in a Soxhlet extractor. A portion of this polymer was then washed with methanol several times, filtered, and dried under vacuum at 50°C. (product a). A second portion

of the polymer, which had been extracted with boiling toluene, was dissolved in boiling N,N-dimethylformamide and precipitated by cooling the solution to room temperature. Polystyrene homopolymer is soluble in N,N-dimethylformamide at room temperature and should have remained in solution. The precipitated polymer was washed with benzene and several times with methanol before it was dried under vacuum at 50°C. (product b). The infrared spectra of products a and b were identical, and the products contained approximately 20 wt.-% polystyrene. Although these experiments do not exclude the presence of homopolymer B, they do support the assumption that bonds were actually formed between A and B sequences.

Similar experiments were carried out on the other copolymers with the use of appropriate solvents.

Properties

The block copolymers of styrene and formaldehyde were capped and stabilized according to the procedures set forth earlier before any physical properties were measured. The final polymers were generally white to off-white in color. Properties depended on both molecular weight and comonomer content. In general, those copolymers containing 20% or less of polystyrene and having an inherent viscosity of 1.0 dl./g. or less were brittle; copolymers in the same composition range, but with inherent viscosities greater than about 1.0 dl./g., tended to be flexible. The distinction between flexible and brittle was made by a somewhat arbitrary test which involved bending a compression-molded sample having a thick-

TABLE III
Comparative Physical Properties of Formaldehyde Polymers

Property	Polymers		
	Block copolymer[a]	Celcon (M-25)	Delrin (500X)
Tensile (at break), psi	9,900	7,500	10,000
Elongation, %	26	43	33
Stiffness, psi	344,000	230,000	342,000
Tensile impact energy, ft.-lb.	0.20–0.21	0.46–0.48	0.20–0.40[b]
Moisture absorption (24 hr.), wt.-%[c]	0.57	0.51	0.49
Moisture absorption (70 hr.), wt.-%	0.86	0.86	0.81
Mold shrinkage, in./in.	0.033	—	0.030
Density (25°C.), g./cc.	1.38	1.41	1.42
Barcol hardness	79–80	70–72	78–79

[a] Contained 7.5 wt.-% styrene.
[b] Samples varied widely.
[c] Run at ambient temperature.

ness of about 0.25 mm. to a 45° angle.   The brittle specimens broke while the flexible ones remained intact.

The physical properties of a styrene (7.5%)–formaldehyde block copolymer and two commercial polyoxymethylene polymers, Celcon and Delrin, are recorded in Table III.   The properties were measured on samples which were injection-molded in a Mini-Jector at 195°C.   The block copolymer had tensile and stiffness properties more like Delrin, a formaldehyde homopolymer, than Celcon, reportedly a random copolymer of trioxane and ethylene oxide.   These results are in accord with what one would expect, i.e., the block copolymer behaved more like the homopolymer than the random copolymer.

OTHER BLOCK COPOLYMERS

Other block copolymers which were prepared are shown in Table IV. The general procedure developed during the work on the styrene–formaldehyde copolymers was closely adhered to in making these polymers. Therefore, unless otherwise specified, the following experiments made use of the techniques already described above for A–B copolymers containing styrene.

TABLE IV
Block Copolymers of Formaldehyde

Comonomer	Block copolymer type	Comonomer, wt.-%
Methyl methacrylate	A–B	5.8
n-Butyl methacrylate	A–B	9.8, 10.5, 11.8
Acrylonitrile	A–B	5.8
Isoprene	A–B	6, 20
N,N-Di-n-butyl acrylamide	A–B	6.2
Styrene (A), phenyl isocyanate (C)	A–(B–C)	5.1(A), 6.0(C)
Styrene	B–A–B	6.2
α-Methylstyrene	B–A–B	7.3

Methyl Methacrylate

Several block copolymers of methyl methacrylate and formaldehyde were prepared using 9-fluorenyllithium as the initiator.   The procedure for the preparation of the poly(methyl methacrylate) block was essentially the one described by Glusker et al.[12]   These workers found that in some instances they were able to maintain essentially 100% of the polymeric chains in a living state.   The specific conditions used in this work varied from experiment to experiment, but can be illustrated by the following. The polymerization of methyl methacrylate (22.0 ml.) in 50 ml. of toluene was initiated at −60°C. by 13 ml. of a 0.25N solution of 9-fluorenyllithium in ethyl ether.   The solution turned green and immediately became viscous.   After stirring for 80 min., formaldehyde was introduced

into the reactor. The color faded to light yellow. Toluene, 900 ml., was added, and formaldehyde addition was continued for 230 min. while maintaining the reaction temperature between -55 and $-63°C$. The product was filtered, washed with methanol, and dried *in vacuo* at 50°C. The yield was 28.4 g. After acetylation, the product was found to contain 41.16% carbon which is equivalent to 5.8% methyl methacrylate. The homopolymer of methyl methacrylate was shown to be soluble in the acetylation mixture and, if present, was assumed to be removed during the acetylation step.

n-Butyl Methacrylate

Although no literature reference to the anionic polymerization of butyl methacrylate was found, this monomer was assumed to undergo "living" polymerization. Indeed, this methacrylate ester polymerized well under the same conditions used for methyl methacrylate and in three runs yielded copolymers containing 9.8, 10.5, and 12.0% by weight of butyl methacrylate.

Acrylonitrile

The acrylonitrile block was prepared by the method of Miller,[16] who has shown that at $-78°C$. in toluene this monomer polymerized to high molecular weight polymer when initiated by *n*-butyllithium. No evidence of chain termination by monomer was found. Hence, under these conditions acrylonitrile formed a "living" polymer and should be capable of initiating formaldehyde polymerization. The copolymerization was carried out in toluene at $-78°C$. according to the general method outlined previously. The white polymer (34 g.) which was isolated contained 1.68% nitrogen which is equivalent to 6.4% of acrylonitrile. Extraction with N,N-dimethylformamide, a solvent for polyacrylonitrile at room temperature, left a product containing 1.54% nitrogen. This is equivalent to 5.8% of acrylonitrile. The presence of the nitrile was confirmed by an infrared absorption band at 4.45 μ.

Isoprene

Isoprene can be polymerized with *n*-butyllithium. Block copolymers of isoprene and styrene have been prepared and thoroughly studied.[17-19] The isomeric distribution one obtains when isoprene is polymerized with *n*-butyllithium varies with the reaction solvent,[20] tetrahydrofuran giving a mixture of isomers. Two experiments were carried out in tetrahydrofuran yielding copolymers containing 6 and 20% isoprene after extraction with hot toluene.

N,N-Di-n-butylacrylamide

The polymerization of N,N-di-*n*-butylacrylamide with ethyllithium was demonstrated by Butler et al.[21] We have confirmed this homopolymerization using *n*-butyllithium as initiator and *n*-heptane as the reaction me-

dium. A block copolymer with formaldehyde was prepared under the same conditions. The product (18.2 g.) contained 6% N,N-di-n-butyl-acrylamide as calculated from nitrogen analysis. The presence of an amide was confirmed by a band appearing in the infrared spectrum at 6.1 μ.

Styrene–Formaldehyde–Phenyl Isocyanate

Isocyanates are known to copolymerize in a random fashion with mono-meric formaldehyde in an anionic system.[22,23] n-Butyllithium will initiate this reaction. Thus, a copolymer containing a block of styrene followed by a block of random formaldehyde–isocyanate units should be obtainable. Such a copolymer was prepared as follows.

The styrene block was prepared from 6.0 g. of styrene monomer in ben-zene as discussed previously. After 40 min. reaction time, formaldehyde gas was introduced into the reactor. After 5 min. the reaction mixture was diluted to 1 liter with benzene and addition of a solution of 2.0 ml. of phenyl isocyanate in 40 ml. of benzene was begun as the solution was cooled to 10°C. The phenyl isocyanate and formaldehyde were added continuously over a period of 165 min. after which time the solvent was removed under an inert atmosphere by means of a filter "stick." One liter of fresh benzene was added to remove unreacted isocyanate and the mixture was filtered again before the polymer was exposed to the at-mosphere. The yield was 40 g. of a white polymer which, after acetylation in xylene, was found to contain 6.0% of phenyl isocyanate and 5.1% styrene.

B–A–B Type Block Copolymers

By the choice of the proper initiator, certain monomers can be poly-merized in such a fashion as to yield "living" anions at both ends of a chain.[2] Such polymeric dianions should be capable of initiating the poly-merization of formaldehyde resulting in a B–A–B type block copolymer. Two such copolymers were prepared, one where the A unit was polystyrene and a second where it was poly-α-methylstyrene.

Styrene

Extreme care must be taken to remove all moisture and oxygen from the system in order to maintain a "living" polystyrene dianion when initiated by sodium naphthalenide. The reactor was assembled and flamed under an argon flow just prior to use. Freshly distilled tetrahydrofuran (60 ml.) was added to the reactor followed by 20 ml. of a $0.1N$ solution of sodium naphthalenide. The solution was cooled to -60°C., and 10 ml. of styrene monomer was added. Formation of the characteristic deep-red color and an increase in viscosity were noted immediately. After 15 min., formal-dehyde gas was introduced into the reactor; in about 2 min., the color faded to clear. After an additional 2 min. the reaction mixture was diluted to 1 liter with toluene, and the formaldehyde polymerization was allowed

to continue for 160 min. at $-60°C$. The yield of polymer was 19.8 g.; an acetylated sample was found to contain 6.2% styrene.

α-Methylstyrene

Homopolymerization of this monomer has been studied by a number of workers.[24,25] A copolymer of the B–A–B type containing 7.3% α-methylstyrene was prepared as follows. Tetrahydrofuran (50 ml.) was distilled from sodium hydride under an argon atmosphere into the reactor. Purified α-methylstyrene (10.0 ml.) was added by means of a syringe and the solution was cooled to $-5°C$. Sodium naphthalenide (10 ml. of a $0.1N$ solution in tetrahydrofuran) was added, causing the solution to become dark red. At this temperature, an equilibrium exists between monomer and polymer such that most of the α-methylstyrene is present as monomer and no catalyst remains unreacted. The solution was then cooled to $-60°C$. and stirred for 1 hr., during which time the α-methylstyrene polymerized, causing an increase in viscosity. Below $-50°C$. the equilibrium

TABLE V
Block Copolymer Properties

Comonomer (and content, wt.-%)	Color	Inherent viscosity, dl./g.	Barcol hardness	k_{222}	Flexible
Styrene (5.1), phenyl isocyanate (6.0)	White	1.16	75	0.28	—
Methyl methacrylate (0.4)	White	—	—	—	—
Methyl methacrylate (5.8)	White	1.35	74–78	0.34	Yes
Styrene (1.0)	White	1.63	—	0.264	—
α-Methylstyrene (7.3)	White	1.65	77	0.082	Yes
Acrylonitrile (5.8)	Lt. yellow	—	82–85	—	—
Styrene (3.2)	White	1.34	78–80	0.084	Yes
Styrene (5.6)	White	0.62	—	—	Yes
Styrene (6.2)	White	—	80–81	—	Yes
n-Butyl methacrylate (9.8)	White	0.70	76–79	0.216	Yes
n-Butyl methacrylate (12.0)	White	0.74	69–71	0.061	Yes
Methyl methacrylate (15.8)	White	0.93	79–80	—	Yes
n-Butyl methacrylate (10.5)	White	Insol.	75–76	0.20	Yes
Isoprene (20.2)	White	—	—	—	No
N,N-Di-n-butyl (6.2)	White	Insol.	70	0.20	Yes
Delrin	White	0.66	79	0.015	Yes
Celcon	White	0.61	70–72	0.002	Yes

shifts, and thus very little monomer remained.   At this time, formaldehyde gas was introduced, causing the red color to dissipate in about 60–90 sec. A great increase in viscosity was noted at this time.   Dry benzene (900 ml.) was then added, causing the temperature to increase to 8°C.   The formaldehyde stream was continued for 145 min., after which the polymer was collected and washed.   The yield was 29.5 g.

Polymer Properties

The properties of block copolymers other than the styrene A–B polymers have not been closely examined.   Only a few runs of an exploratory nature were made with each comonomer.   Most of the properties which could be measured on small samples are listed in Table V.   In general, the copolymers were white, the only exception being the acrylonitrile polymer which yellowed slightly during acetylation.   Flexibility was good except in the case of an isoprene copolymer which contained a large amount of isoprene. Polymers containing n-butyl methacrylate remained flexible up to at least 12 wt.-%.   Surface hardness, as measured by the Barcol hardness tester, shows the block copolymers to be as hard or harder than the homopolymer (Delrin) up to about 10 wt.-% comonomer.   This is apparently true even for a "soft" monomer like n-butyl methacrylate.   The copolymer containing 6.2 wt.-% N,N-di-n-butylacrylamide appears to be an exception, possibly because some random copolymerization occurred.

The methacrylate and styrene block copolymers gave clear moldings when compression-molded about 10°C. below their softening points. These clear moldings were harder and more brittle than samples molded above the softening points.

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Résumé

Des mesures de solubilité et de spectroscopie confirment la formation de copolymères séquencés A–B entre des monomères subissant la polymérisation anionique (unités A) et le formaldéhyde monomère (unités B). Les comonomères envisagés dans cette étude étaient le styrène, le méthacrylate de méthyle et le méthacrylate de *n*-butyle, l'acrylonitrile, l'isoprène et l'acrylamide *N,N*-di-*n*-butylée. On montre également la formation de copolymères B–A–B entre le styrène et l'α-méthylstyrène et le formaldéhyde; on a également préparé un copolymère statistique A–(B–C) de styrène, formaldéhyde et d'isocyanate de phényle (*C*). Les détails expérimentaux de la préparation de formaldéhyde monomérique de haute pureté, se prêtant à un tel travail, est décrit avec certains détails. On insiste sur le fait que cette étude était primitivement destinée à montrer qu'il était possible de préparer des copolymères séquencés de formaldéhyde; c'est pour cela qu'un travail ultérieur est indispensable pour mieux fixer la nature quantitative ce ces réactions.

Zusammenfassung

Löslichkeitsdaten und spektroskopische Ergebnisse sprechen für die Bildung von A–B-Blockcopolymeren zwischen monomerem Formaldehyd (B-Bausteine) und Monomeren (A-Bausteine) bei der anionischen Polymerisation. Als Comonomere wurden verwendet: Styrol, Methyl- und *n*-Butylmethacrylat, Acrylnitril, Isopren und *N,N*-Di-*n*-butylacrylamid. Ähnliche Ergebnisse wurden bezüglich der Bildung von B–A–B-Copolymeren zwischen Styrol, α-Methylstyrol und Formaldehyd erhalten; schliesslich wurde auch ein statistisches A–(B–C)-Copolymeres von Styrol, Formaldehyd und Phenylisocyanat hergestellt. Experimentelle Details für die Darstellung von hochgereinigtem, monomerem Formaldehyd, wie er für solche Versuche erforderlich ist, werden genau beschireben. Es wird betont, dass die vorliegende Untersuchung vor allem die prinzipielle Möglichkeit der Darstellung von Formaldehydblockcopolymeren zeigen sollte; es sind daher noch weitere Versuche notwendig, um die quantitativen Verhältnisse bei diesen Reaktionen aufzuklären.