

Polystyrene Modifications. II. Ring-Substituted Polystyrenes*

K. R. DUNHAM, J. W. H. FABER, J. VANDENBERGHE, and W. F. FOWLER, JR., *Kodak Research Laboratories, Eastman Kodak Company, Rochester, New York*

INTRODUCTION

In Part I the improvements in thermal properties of poly(styrene-co-acenaphthylene) were reported.¹ Terpolymers based on poly(styrene-co-acenaphthylene) were flexible but they had low glass transition temperatures (T_g), were generally incompatible, and crazed readily. The present paper will deal with studies of thermal properties and crystallinities of ring-substituted polystyrenes.

DISCUSSION

Inherent viscosities and T_g 's of monosubstituted polystyrenes are listed in Tables I and II, those of disubstituted polystyrenes in Tables III-V.

Monosubstitution of methyl groups or chlorine atoms in the ortho position of polystyrene raised T_g , while meta substitution reduced T_g . Para

TABLE I
Glass Transition Temperatures of Poly(monomethylstyrene)

Compound	$\{\eta\}$	T_g , °C.
Polystyrene	0.78	101
Poly(2-methylstyrene)	1.85	135.5
Poly(3-methylstyrene)	0.65	97
Poly(4-methylstyrene)	3.37	93

TABLE II
Glass Transition Temperatures of Poly(monohalostyrene)

Compound	$\{\eta\}$	T_g , °C.
Poly(2-chlorostyrene)	2.35	119
Poly(3-chlorostyrene)	1.96	90
Poly(4-fluorostyrene)	2.02	83, 106
Poly(4-chlorostyrene)	2.46	116
Poly(4-bromostyrene)	2.26	144

* Communication No. 2260 from the Kodak Research Laboratories.

TABLE III
Glass Transition Temperatures of Poly(dimethylstyrene)

Compound	{ η }	T_g , °C.
Poly(2,5-dimethylstyrene)	3.40	143
Poly(2,4-dimethylstyrene)	1.54	112
Poly(3,4-dimethylstyrene)	Insoluble	107, 111

TABLE IV
Glass Transition Temperatures of Poly(dihalostyrenes)

Compound	{ η }	T_g , °C.
Poly(4-chloro-3-fluorostyrene)	Insoluble	122
Poly(3,4-dichlorostyrene)	0.92	128
Poly(2,5-dichlorostyrene)	1.36	106
Poly(2,4-dichlorostyrene)	1.02	135

TABLE V
Glass Transition Temperatures of Disubstituted Polystyrenes

Compound	{ η }	T_g , °C.
Poly(4-chloro-3-methylstyrene)	2.27	114
Poly(4-chloro-2-methylstyrene)	0.58	145
Poly(2-methyl-5- <i>tert</i> -butylstyrene)	1.54	87

monohalo substitution caused increased T_g 's with increasing size of the substituted halogen, while para monomethyl substitution reduced T_g . Except for poly(*p*-methylstyrene), these results are in general accord with observations made by Barb² on softening points of substituted polystyrenes, although T_g values assigned by our measurements differ somewhat from Barb's reported softening points for corresponding polymers.

Disubstituted polystyrenes generally had T_g 's higher than that of polystyrene; the only exception found was that of poly(2-methyl-5-*tert*-butylstyrene), which had a T_g of 87°C. Two T_g values were obtained for poly(3,4-dimethylstyrenes) prepared with different catalysts—111°C. for an amorphous emulsion-polymerized sample and 107°C. for an $\text{Al}(\text{C}_2\text{H}_5)_3$ - VCl_3 -catalyzed polymer. X-ray diffraction photographs showed the latter polymer to be moderately crystalline.

Monosubstitution of chlorine atoms in the polystyrene ring produced effects on T_g different from corresponding methyl substitution. Compared with the T_g of polystyrene, meta chloro substitution lowered T_g 11°; meta methyl substitution lowered it 4°. The para chloro polymer had a T_g 15° above that of polystyrene, while a para methyl group reduced the T_g 8°. Ortho substitution increased T_g , the increase with a methyl group being 34.5° and that with a chloro group 18°C.

The different effects of methyl substitution and chloro substitution were also observed in disubstituted polystyrenes (Tables III and IV). The T_g 's of the 3,4-disubstituted polymers were higher than those of the correspond-

ing 3- or 4-monosubstituted derivatives. The T_g of poly(3,4-dichlorostyrene) was 21° higher than that of poly(3,4-dimethylstyrene), while the T_g of poly(2,5-dichlorostyrene) was 37° below that of the corresponding dimethyl polymer. The T_g of the 2,4-dichloro derivative, 135°C., was 23° above that of poly(2,4-dimethylstyrene).

The T_g 's of dichloro- and chloromethyl-substituted polystyrenes appeared to be additive functions of the T_g 's of the corresponding monosubstituted derivatives. If the 101°C. T_g of polystyrene is established as a reference point, a value for each monosubstituted group or atom can be assigned according to the amount it raises or lowers T_g . Ortho chloro substitution then could be assigned a value of +18°C. (T_g of poly(2-chlorostyrene) 18° above that of polystyrene), while meta chloro substitution would be assigned a value of -11°C. (T_g of poly(3-chlorostyrene) equals 90°C.) Addition of these values establishes a calculated T_g of 108°C. for poly(2,5-dichlorostyrene). As seen in Table VI, the calculated T_g 's of disubstituted polymers containing chlorine agree closely with observed values except for poly(3,4-dichlorostyrene). No such correlation was observed in the dimethyl series.

TABLE VI
Calculated and Observed Glass Transition Temperatures of Poly(chlorostyrenes)

Substituents	Obsd. T_g , °C.	Calcd. T_g , °C.
2,5-Dichloro	106	108
2,4-Dichloro	135	134
3,4-Dichloro	128	105
4-Chloro-3-methyl	114	112
4-Chloro-2-methyl	145	151

The calculation appears to be valid for 3,4-disubstituted polystyrenes if the T_g differences between monosubstituted derivatives are added without regard to sign. The T_g 's calculated in this manner agree closely with observed values, as shown in Table VII. If examination of other orthodisubstituted polystyrenes should show general agreement between observed T_g 's and T_g 's calculated in this manner, it would indicate strong interference between the orthosubstituted groups. It is suggested that energies normally leading to mobility in the monosubstituted group or atom are utilized to form weak bonds between adjacent orthosubstituted groups or atoms, reducing their mobility.

It would be desirable to test the above calculations on other substituted polystyrenes to determine whether they can be applied generally in calculating T_g .

Crystallinities of polymers prepared with stereoregulating catalysts were measured by x-ray diffraction. Poly(2,4-dimethylstyrene), prepared with the $\text{Al}(\text{C}_2\text{H}_5)_3\text{-VCl}_2$ catalyst, was more amorphous than the crystalline polymer prepared by Natta et al.³ with a different catalyst. Since poly(*o*-vinyltoluene) prepared with the vanadium catalyst is crystalline, it is

TABLE VII
Calculated and Observed Glass Transition Temperatures of (3,4-disubstituted Polystyrenes)

Substituent	ΔT_{gv} , °C. ^a	ΔT_{gv} , °C. ^b	101 + ΔT_{gv} , °C.	Obsd. T_g , °C.
3,4-Dichloro	11	15	127	128
3,4-Dimethyl	4	8	113	107, 111
4-Chloro-3-methyl	4	15	120	114

^a Difference in T_g of 3-monosubstituted derivative from that of polystyrene.

^b Difference in T_g of 4-monosubstituted derivative from T_g of polystyrene.

evident that the parasubstituted methyl group in poly(2,4-dimethylstyrene) prevented crystallization. Poly(3,4-dimethylstyrene), however, prepared under the same conditions, is crystalline, demonstrating the effect of metasubstitution in overcoming retardation of crystallinity by the parasubstituted group.

Natta has disclosed that monosubstitution of an atom or group larger than fluorine in the para position prevents it from crystallizing. Sianesi et al.⁴ prepared crystalline disubstituted polystyrenes in which the para position is occupied, using $\text{Al}(\text{C}_2\text{H}_5)_3\text{-TiCl}_4$ as catalyst. Poly(3,4-dimethylstyrene), for example, is described as being crystalline and having a melting point of 240°C. The work of Natta et al.³ demonstrated that retardation of crystallization by monosubstitution in the para position of isotactic polystyrene could be partially overcome by further substitution in other positions.

Cast sheets of modified polystyrenes were flexed and examined visually for crazing. In Table VIII, polymers are divided into two groups according to their crazing properties; it will be noted that none show improvement over polystyrene. The high T_g 's of the majority of these polymers establish them as rigid nonmobile systems.

The mechanical properties of oriented monofilaments of poly(2-methylstyrene) and poly(3,4-dichlorostyrene) are listed in Table IX. Yield and tensile strengths of poly(2-methylstyrene) and poly(3,4-dichlorostyrene)

TABLE VIII
Crazing in Flexed 4-Mil Sheets of Amorphous Unoriented Substituted Polystyrenes

Craze more readily than polystyrene	Craze same as polystyrene
Poly(2,5-dimethylstyrene)	Poly(<i>o</i> -vinyltoluene)
Poly(2-methyl-5- <i>tert</i> -butylstyrene)	Poly(<i>p</i> -fluorostyrene)
Poly(4-methylstyrene)	Poly(3-methylstyrene)
Poly(vinylcyclohexane)	Poly(4-chloro-3-methylstyrene)
Poly(<i>p</i> -chlorostyrene)	Poly(3-phenylpropene-1)
Poly(<i>p</i> -bromostyrene)	Poly(3,4-dimethylstyrene)
Poly(2,5-dichlorostyrene)	Poly(3,4-dichlorostyrene)

TABLE IX
Mechanical Properties of Oriented Hydrophobic Polymers

Polymer	Moisture absorption	Young's modulus, $\times 10^{-4}$ kg./cm. ²	Yield point, kg./cm. ²	Tensile strength, kg./cm. ²	Elong. at break, %	T_g , °C.	Heat distortion temp., °C.
Monofil, Koppers atactic, stretched 210% at 110°C.	0.01	3.4	630	810	>4	100	100
Plax PD, biaxially oriented polystyrene sheet	0.01	3.5	—	810	3.6-4	100	100
Poly(2-methylstyrene)	0.01	4.1	705	705	3	135.5	119
Poly(3,4-dichloro-styrene), stretched 150% at 160°C.	0.01	4.1	—	855	2.3	128	—
4M4 butyrate sheet	3.2	2.8	—	685	28	—	130
G.E. Lexan polycarbonate	0.3	2.8	510-630	630-738	60-100	—	High

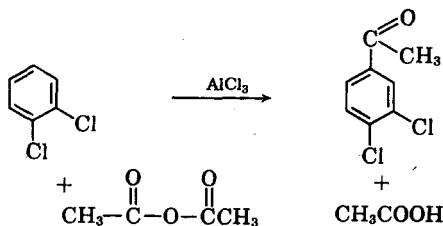
compare favorably with those of polystyrene, while the moduli and thermal properties of the substituted polymers are superior.

The substituted polystyrenes also compare favorably with Lexan polycarbonate and 4M4 butyrate sheet in mechanical properties and have superior Young's moduli and moisture absorption.

EXPERIMENTAL

I. Substituted Acetophenones

A. Preparation of:

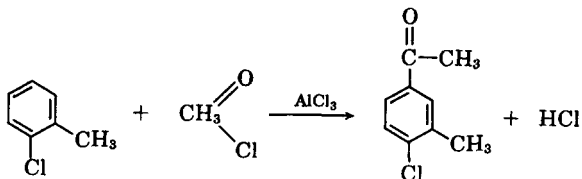


The procedure of Stempel et al.⁵ was used in preparing 3,4-dichloroacetophenone and 4-chloro-3-fluoroacetophenone. The yield of 3,4-dichloroacetophenone was 93.8% of the theoretical amount (based on starting weight of acetic anhydride), b.p. 127–132°C. at 10 mm., m.p. 73°C.

In the preparation of 4-chloro-3-fluoroacetophenone, *o*-chlorofluorobenzene was heated to 70°C. and the aluminum chloride was then added slowly. The conversion to 4-chloro-3-fluoroacetophenone was 50% of the theoretical (based on starting weight of acetic anhydride), b.p. 120°C. at 10 mm. pressure.

ANAL. Calcd.: C 50.8, H 3.1, Cl 38.0. Found: C 50.0, H 2.9, Cl, 37.1.

B. Preparation of:



A modification of procedure IA was used for 4-chloro-3-methylacetophenone, 6-acetyl-1,2,3,4-tetrahydronaphthalene, 5-acetyllindane, 4-chloro-2-methylacetophenone, and 2,4,6-trimethylacetophenone. This method, reported by Mowry et al.,⁶ consisted in adding a substituted benzene to a preformed complex of acetyl chloride–aluminum trichloride in an inert solvent.

4-Chloro-3-methylacetophenone distilled at 16 mm. pressure, b.p. 128–130°C. Conversion was 70% of the theoretical, based on substituted benzene starting material.

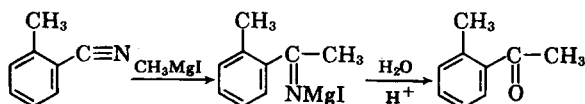
6-Acetyl-1,2,3,4-tetrahydronaphthalene was prepared at -5°C ., with no heating following addition of acetyl chloride. Conversion was 480 g. (91.5% of theoretical yield), b.p. 108°C. at 0.8 mm.

5-Acetyllindane: b.p. 132–134°C. at 12 mm., conversion 33.6% of the theoretical.

4-Chloro-2-methylacetophenone: b.p. 272°C., conversion 18.6%.

2,4,6-Trimethylacetophenone: b.p. 100–102°C. at 10 mm., conversion 33.9%.

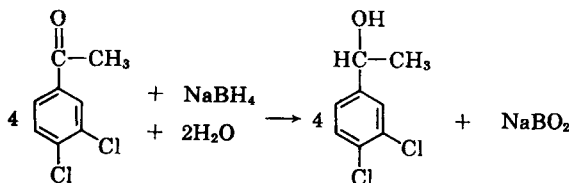
C. Preparation of:



Into a 22-l. flask equipped with a stirrer, a reflux condenser, and a drying tube, was placed 408 g. (17 g.-atoms) of magnesium turnings. A few drops of methyl iodide were added to start the reaction. Anhydrous ether, 4 l., was then poured into the flask, and methyl iodide, 2414 g. (17 moles) in 1200 ml. of ether, was added slowly over a 4-hr. period. The mixture was stirred another $\frac{1}{2}$ hr. and 1989 g. (17 moles) of *o*-tolunitrile was added over a 25-min. period. After standing overnight, the complex was destroyed by slow addition of water and dilute hydrochloric acid. The ether layer was separated, and the aqueous layer extracted four times with ether. The combined ether layers were washed with water, dried over magnesium sulfate, and distilled. During the first distillation, the product came over as an azeotrope. This was separated and the product redistilled: b.p. 140°C. at 100 mm., conversion 1666 g. (74% of theoretical amount), $d_4^{25} = 1.001$.

II. Secondary Alcohols

A. Preparation of:



A solution of 2 l. of anhydrous methanol and 106 g. (0.56 mole) of 3,4-dichloroacetophenone was poured into a 5-l. flask equipped with thermometer, solids addition tube, stirrer, and reflux condenser. The temperature was increased by rapidly adding sodium borohydride, and gentle reflux was then maintained by slower addition until 19 g. (0.5 mole) had been added.

After refluxing 1 hr. additional, the liquid was poured into 4 l. of water containing 10 ml. of hydrochloric acid. The organic layer was separated, washed twice with water, dried over calcium chloride, filtered, and distilled through a 25-in. column packed with glass helices.

This method was used in preparing the following:

3,4-Dichlorophenylmethylcarbinol
 2,5-Dimethylphenylmethylcarbinol
 3,4-Dimethylphenylmethylcarbinol
 2,4-Dimethylphenylmethylcarbinol
 4-Fluorophenylmethylcarbinol
 4-Chlorophenylmethylcarbinol, b.p. 81–86°C. at 1.0 mm., conversion 90%.

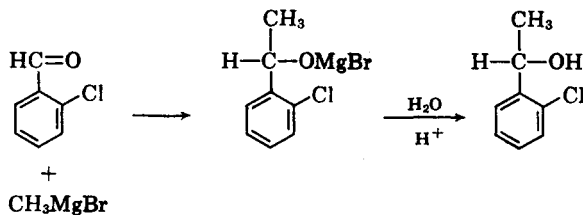
ANAL. Calcd.: C 62.5, H 5.7, Cl 22.7. Found: C 62.8, H 6.0, Cl 23.4.

4-Bromophenylmethylcarbinol, b.p. 130°C. at 12 mm., conversion 90%.

ANAL. Calcd.: C 47.7, H 4.4, Br 39.8. Found: C 48.0, H 4.2, Br 40.2.

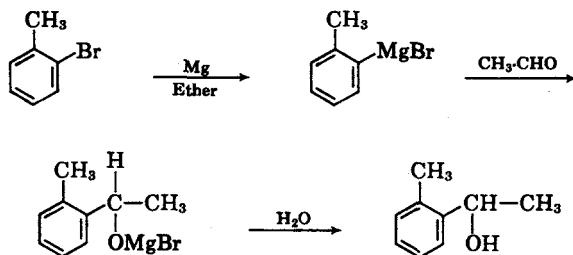
4-Biphenylmethylcarbinol
m-Bromophenylmethylcarbinol

B. Preparation of 2-Chlorophenylmethylcarbinol



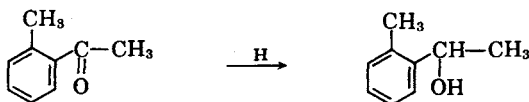
In a 3-l. flask equipped with thermometer, stirrer, dropping funnel, and effective reflux condenser were placed 140 g. (1.0 mole) of *o*-chlorobenzaldehyde and 500 g. of dry ether. The flask was placed in a cooling bath in a dry box filled with dry nitrogen. The stirrer was started and 266.5 cc. (1.0 mole) of a solution of methylmagnesium bromide in ether was slowly added to maintain a gentle reflux. After the addition was completed, stirring was continued for 1 hr.

The reaction mixture was poured into 2 l. of water containing 10 cc. of concentrated sulfuric acid. The organic layer was washed twice with water, dried over calcium chloride, and filtered. The ether was removed on a steam bath and the product distilled: b.p. 120°C. at 27 mm., conversion 87 g. (56%).

*C. Preparation of o-Methylphenylmethylcarbinol***Preparation 1**

In a 4-l. flask equipped with thermometer, efficient reflux condenser with drying tube, stirrer, and dropping funnel were placed 29.4 g. (1.2 g.-atoms) of magnesium turnings, 3 l. of ether, and a crystal of iodine. Slowly, 171 g. (1.0 mole) of *o*-bromotoluene was added, a gentle reflux being maintained. Refluxing was continued for 2 hr. additional, the solids were allowed to settle, and the Grignard solution was carefully decanted into another 5-l. flask in a dry box. The 5-l. flask was placed in a cooling bath containing sodium chloride and ice. When the temperature of the Grignard solution reached 0°C., 44 g. (1.0 mole) of acetaldehyde was dropped in slowly, to maintain a temperature of 0°C.

The temperature was slowly raised to room temperature and the reaction mixture was poured onto 2 l. of water containing 10 cc. of concentrated sulfuric acid. The organic layer was separated, washed twice with water, dried over calcium chloride, and filtered. Ether was driven off on a steam bath and the product was distilled: b.p. 110°C. at 10 mm., conversion 66.5%.

Preparation 2

o-Methylacetophenone was catalytically hydrogenated. The reaction mixture was filtered, and alcohol removed by distillation, under vacuum. The product was distilled through a 12-in. Vigreux column, giving two fractions.

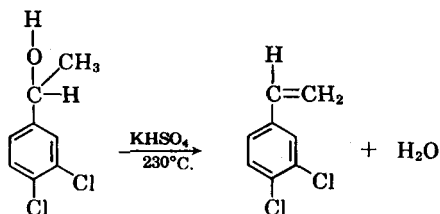
Fraction 1: b.p. 122°C. at 50 mm., $d_4^{27} = 1.008$, $n_D^{25} = 1.5293$.

Fraction 2: b.p. 133°C. at 50 mm., $d_4^{27} = 1.008$, $n_D^{25} = 1.5298$.

Fraction 1 was redistilled through a 12-in. column packed with glass helices to give unreacted ketone and a product boiling at 132.5–133°C., $n_D^{25} = 1.5296$, conversion 77%.

III. Substituted Vinyl Compounds

The preparation of 3,4-dichlorostyrene illustrates the procedure employed.



In a 200-ml. flask equipped with a thermometer reaching to within $\frac{1}{8}$ in. of the bottom, a take-off head, and a pressure-equalizing dropping funnel was placed 12 g. of potassium acid sulfate. In the dropping funnel was placed 38.2 g. of 3,4-dichlorophenylmethylcarbinol. The system was evacuated to 80 mm. Hg, the flask heated at 230°C . to melt the potassium acid sulfate, and 3,4-dichlorophenylmethylcarbinol added slowly. The rate of addition was such that it equalled the take-off rate of 3,4-dichlorostyrene-water (azeotrope). Temperature was maintained between 210 and 250°C . and pressure was held constant at 80 mm. The dichlorostyrene-water azeotrope distilled at 140 – 150°C .

The distillate was diluted with an equal amount of ether, placed in a freezer overnight, and the ether solution decanted from ice. A few crystals of *tert*-butyl pyrocatechol were added, the ether was driven off, and the 3,4-dichlorostyrene was distilled: conversion 68% (23.5 g.), b.p. 77 – 79°C . at 1.5 mm.

The following vinyl compounds were prepared in the same manner with slight variations as indicated:

2,5-Dimethyl styrene: conversion 86%, b.p. 82 – 83°C . at 23 mm.

3,4-Dimethyl styrene: conversion 80%, b.p. 94 – 96°C . at 26 mm.

p-Fluorostyrene: conversion 70%, b.p. 66 – 68°C . at 10 mm.; dehydration was carried out at atmospheric pressure.

p-Chlorostyrene: conversion 73%, b.p. 53 – 54°C . at 3 mm.; dehydration was carried out at atmospheric pressure.

p-Bromostyrene: conversion 72%, b.p. 87 – 88°C . at 12 mm.; pressure during dehydration, 100 mm.

3-Chloro-4-fluorostyrene: conversion 60%, b.p. 70 – 73°C . at 10 mm.; pressure 25 mm., distillation temperature 100°C .

2,4-Dichlorostyrene: conversion 75.5%, b.p. 52°C . at 1 mm.

2,4-Dimethylstyrene: conversion 44.9%, b.p. 38°C . at 1 mm.

ANAL. Calcd.: C 89.9, H 9.1. Found: C 90.2, H 9.3.

- 4-Chloro-3-methylstyrene: conversion 61%, b.p. 53°C. at 1.0 mm.
2-Chloro-5-methylstyrene: conversion 29%, b.p. 37-39°C. at 1.5 mm.
4-Chloro-2-methylstyrene: conversion 70%, b.p. 88-90°C. at 10 mm.
o-Chlorostyrene: conversion 70%, b.p. 69°C. at 10 mm.
o-Vinyltoluene: conversion 87.9%, b.p. 55°C. at 10 mm.

IV. Emulsion Polymerization of Monomers

Monomer in a 10-g. amount, 24 ml. of distilled water, 0.4 g. of *N*-oleoyl-*N*-methyltauramide, 0.1 g. of potassium metabisulfite, and 0.2 g. of potassium persulfate were placed in a 4-oz. pressure bottle. The bottle was flushed with nitrogen, capped, and tumbled in a 30°C. water bath for 44 hr. The polymerized samples were poured into half-pint freezer cartons and frozen at -20°C. to break the emulsions. After thawing, the polymers were filtered, washed with water until no foam appeared in the filtrate, and then washed with methanol. The granular polymers were dried in a vacuum oven at 30°C.

Analyses

- Poly(*p*-bromostyrene). Calcd.: C 52.4, H 3.8. Found: C 52.8, H 4.1.
Poly(*p*-methylstyrene). Calcd.: C 91.6, H 8.4. Found: C 91.3, H 8.8.
Poly(2-chlorostyrene). Calcd.: C 69.1, H 5.1. Found: C 69.7, H 5.6.
Poly(4-chlorostyrene). Calcd.: C 69.1, H 5.1, Cl 25.6. Found: C 69.1, H 5.2, Cl 26.0.
Poly(4-chloro-3-fluorostyrene). Calcd.: C 61.2, H 4.4, Cl 22.4, F 12.0. Found: C 61.3, H 3.9, Cl 22.3, F 12.7.
Poly(2,5-dichlorostyrene). Calcd.: C 55.5, H 3.5, Cl 41.0. Found: C 54.9, H 3.4, Cl 39.3.
Poly(2,5-dichlorostyrene). Calcd.: C 55.5, H 3.5, Cl 41.0. Found: C 55.7, H 3.8, Cl 40.8.
Poly(3,4-dichlorostyrene). Calcd.: C 55.5, H 3.5, Cl 41.0. Found: C 55.7, H 3.8, Cl 41.2.
Poly(2,4-dichlorostyrene). Calcd.: C 55.5, H 3.5, Cl 41.0. Found: C 55.2, H 3.6, Cl 41.1.
Poly(2,5-dimethylstyrene). Calcd.: C 90.9, H 9.1. Found: C 91.3, H 9.0.
Poly(4-chloro-3-methylstyrene). Calcd.: C 70.8, H 6.0, Cl 23.2. Found: C 71.1, H 6.2, Cl 23.6.
Poly(4-chloro-2-methylstyrene). Calcd.: C 70.8, H 6.0, Cl 23.2. Found: C 70.8, H 6.0, Cl 23.1.
Poly(3-methylstyrene). Calcd.: C 91.6, H 8.4. Found: C 89.5, H 7.8.
Poly(3,4-dimethylstyrene). Calcd.: C 90.9, H 9.1. Found: C 88.1, H 9.1.

V. Determination of Glass Transition Temperatures

The T_g 's were obtained by differential thermal analysis.

CONCLUSIONS

Substituents in the aromatic ring of polystyrene has been observed to influence T_g , the profoundness of the effect depending upon the nature, position, and number of substituents. In some multisubstituted polystyrenes, the effects of substituents on T_g may be additive. Severity of crazing is not decreased significantly by ring substitution. The substituted polymers have high Young's moduli, low moisture absorption, and excellent thermal properties.

The contributions of S. E. Petrie, L. Contois, and J. Kane, who provided physical measurements, are gratefully acknowledged.

References

1. Dunham, K. R., J. VanDenBerghe, and J. W. H. Faber, *J. Appl. Polymer Sci.*, in press.
2. Barb, W. G., *J. Polymer Sci.*, **37**, 515 (1959).
3. Natta, G., F. Danusso, and D. Sianesi, *Makromol. Chem.*, **28**, No. 3, 253 (1958).
4. Sianesi, D., G. Natta, and F. Danusso, *Gazz. chim. ital.*, **89**, No. 3, 775 (1959).
5. Stempel, G. H., Jr., C. Greene, R. Rongone, B. Sobel, and R. Odioso, *J. Am. Chem. Soc.*, **73**, 455 (1951).
6. Mowry, D. T., M. Renoll, and W. F. Huber, *J. Am. Chem. Soc.*, **68**, 1105 (1946).

Synopsis

Ring-substituted styrenes were prepared and polymerized. They usually had higher glass transition temperatures than polystyrene. In some disubstituted systems the T_g was an additive function of the individual groups. Crystallinities of methyl-substituted polymers varied, depending upon the ring positions involved. Crazing tendencies were equivalent to those in polystyrene.

Résumé

On a préparé et polymérisé des styrènes substitués dans le noyau. Ces polymères ont en général des températures de transition vitreuse plus élevées que le polystyrène, quoiqu'on ait trouvé quelques exceptions. Dans certains systèmes disubstitués, la T_g était une fonction additive des groupes individuels. Les cristallinités des polymères à substituant méthyle variaient suivant les positions occupées dans le noyau. Les tendances au fendillement superficiel étaient équivalentes à celles du polystyrène.

Zusammenfassung

Ringsubstituierte Styrole wurden dargestellt und polymerisiert. Die Polymeren besaßen im allgemeinen höhere Glasumwandlungstemperaturen als Polystyrol; einige Ausnahmen wurden gefunden. Bei einigen disubstituierten Substanzen war T_g eine additive Funktion der einzelnen Gruppen. Die Kristallinität der methylsubstituierten Polymeren zeigte eine Abhängigkeit von der beteiligten Ringstellung. Die Rissbildungstendenz entsprach der des Polystyrols.

Received January 31, 1962