Synthesis and Properties of Regular Copolymers I—Reactions Involving Aliphatic Dihalides

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A method is described for preparing regular copolymers with repeat unit —[M—R—M]—, *where* M *is a vinyl or diene monomer, and* R *is the ligand of an aliphatic dihalide. Over forty polymers of this type are reported and confirmation of their structures is given by n.m.r. analysis. Specific viscosities, measured as one per cent solutions in tetrahydrofuran at 25°C, of up to 0·25 have been obtained with these polymers, but no attempt has been made as yet to maximize the degrees of polymerization. Monomers which undergo this polymerization process include styrene, α-methylstyrene, butadiene and isoprene.*

THE development of the 'living' polymer method of polymerization by M. Szwarc and his school[1,2] has allowed the synthesis of vinyl and diene polymers of well defined structure and controllable terminal groups, and the preparation of certain types of star and comb shaped polymers and a number of block copolymers can now be carried out efficiently. The method, nevertheless, does have the severe practical limitation that it is very sensitive to traces of common impurities such as water and oxygen, so that, for quantitative work, extreme precautions have to be taken to prepare and maintain the materials in a high state of purity. The essential difficulty is that the highly reactive carbanions produced must be preserved during the polymerization stage and until the terminating agent is introduced. Some work has been done, however, with a terminating agent, ethanol, present in the reaction mixture[3] and this confirms that the resulting dimeric hydrocarbon principally formed has a central tail to tail link. Thus, for a vinyl monomer of the form $CH_2{=}CHX$, the initiating dianion is of the form $\bar{C}HX{-}CH_2{-}CH_2{-}\bar{C}HX$.

If, therefore a difunctional reactant is present in an amount equivalent to half the monomer molarity, then regular copolymers should be obtained with the repeat unit —[M—R—M]— where M is the monomer and R is the linking ligand. This approach forms the basis of the method to be described, and the present paper details some of the polymers obtained using aliphatic dihalides as linking agents.

MATERIALS

Monomers

The vinyl monomers used were styrene, methylmethacrylate, α-methylstyrene, β-methylstyrene, *o*-methylstyrene, *m*-methylstyrene, *p*-methylstyrene, 1,1-diphenylethylene, and 4-vinyldiphenyl. The diene monomers used were butadiene and isoprene. The purest commercially obtainable grades were purified where possible by drying with molecular sieves, then calcium hydride, and finally by vacuum distillation immediately before use. Butadiene was dried by distillation from the cylinder through drying tubes containing phosphorus pentoxide and was collected in an evacuated graduated container.

Dihalides

Commercially obtainable dihalides of the best grade were used and purified by vacuum distillation after drying. Some of the materials used are listed in *Tables 1* and *2*.

Table 1

Run	Monomer	*Dihalide** X—R—X *where* R *is*	*Aliphatic/Aromatic* H *ratio*		
			Theory	*Experiment*	*Specific viscosity*
1	styrene	$\cdot CH_2\cdot$	0·82	0·82	0·063
2		$\cdot(CH_2)_2\cdot$	1·0	0·70	0·126
3		$\cdot(CH_2)_3\cdot$	1·2	1·18	0·085
4		$\cdot(CH_2)_4\cdot$	1·4	1·35	0·128
5		$\cdot(CH_2)_5\cdot$	1·6	1·50	0·163
6		$\cdot(CH_2)_6\cdot$	1·8	1·80	0·144
7		$\cdot(CH_2)_{10}\cdot$	2·6	2·50	0·137
8		$\cdot CH(CH_3)(CH_2)_2(CH_3)CH\cdot$	1·8	1·70	0·067
9		*p*. $\cdot CH_2C_6H_4CH_2\cdot$	0·71	0·72	0·096
10		*o*. $\cdot CH_2C_6H_4CH_2\cdot$	0·71	0·69	0·052
11	α-methylstyrene	$\cdot CH_2\cdot$	1·2	1·24	0·045
12		$\cdot(CH_2)_2\cdot$	1·4	1·10	0·127
13		$\cdot(CH_2)_3\cdot$	1·6	1·53	0·099
14		$\cdot(CH_2)_4\cdot$	1·8	1·81	0·120
15		$\cdot(CH_2)_5\cdot$	2·0	2·00	0·143
16		$\cdot(CH_2)_6\cdot$	2·2	2·33	0·149
17		$\cdot(CH_2)_{10}\cdot$	3·0	3·04	0·163
18		*p*. $\cdot CH_2C_6H_4CH_2\cdot$	1·0	0·92	0·108
19		*o*. $\cdot CH_2C_6H_4CH_2\cdot$	1·0	0·95	0·070
20		$(CH_3)_2SiCl_2$	1·6	1·60	—
21	β-methylstyrene	$\cdot(CH_2)_4\cdot$	1·8	1·92	0·118
22	*o*-methylstyrene	$\cdot(CH_2)_4\cdot$	2·5	2·32	0·115
23	*m*-methylstyrene	$\cdot(CH_2)_4\cdot$	2·5	2·55	0·105
24	*p*-methylstyrene	$\cdot(CH_2)_4\cdot$	2·5	2·49	0·126
25	4-vinyldiphenyl	$\cdot(CH_2)_4\cdot$	0·78	0·77	0·077
26	1,1-diphenylethylene	$\cdot(CH_2)_3\cdot$	0·50	0·54	0·088
27	methylmethacrylate	$\cdot(CH_2)_5\cdot$	0·30†	0·29†	—

*All are dibromides unless otherwise stated.
†Ratio of hydrogens of methyl ester to all other hydrogens.

Metal

Sliced and washed lithium rod was employed in the majority of experiments. In some experiments, sliced and washed sodium metal, and in one case a liquid sodium–potassium alloy was used.

Solvents

Tetrahydrofuran, used as solvent for the experiments, was dried over sodium–potassium alloy and distilled before use.

Table 2

Run	*Monomer*	*Dihalide** X—R—X *where* R *is*	*Specific viscosity*	*Aliphatic/Aromatic ratio*		*Form*
				Theory	*Experiment*	
28	butadiene	•(CH_2)•	0·207			Viscous oil
29		•$(CH_2)_2$•	0·163			Viscous oil
30		•$(CH_2)_3$•	0·200			Viscous oil
31		•$(CH_2)_4$•	0·214			Viscous oil
32		•$(CH_2)_5$•	0·178			Viscous oil
33		•$(CH_2)_6$•	0·224			Viscous oil
34		•$(CH_2)_{10}$•	0·166			Viscous oil
35		*p.* •$CH_2C_6H_4CH_2$•	0·217	4·0	3·9	Rubbery solid
36		$ClC(Ph)_2Cl$	0·042	1·2	1·0	Rubbery solid
37	isoprene	•(CH_2)•	0·04			Viscous oil
38		•$(CH_2)_2$•	0·051			Viscous oil
39		•$(CH_2)_3$•	0·057			Viscous oil
40		•$(CH_2)_4$•	0·118			Viscous oil
41		•$(CH_2)_5$•	0·081			Viscous oil
42		•$(CH_2)_6$•	0·072			Viscous oil
43		•$(CH_2)_{10}$•	0·100			Viscous oil
44		*p.* •$CH_2C_6H_4CH_2$•	0·158	5·0	4·6	Rubbery solid
45		$ClC(Ph)_2Cl$	0·042	1·6	1·5	Rubbery solid

*Dibromides unless otherwise stated.

EXPERIMENTAL METHOD

A suspension of lithium metal (about 0·8 mole) in tetrahydrofuran (500 ml) was stirred under nitrogen in a one-litre three necked round bottom flask. After a few minutes a mixture of monomer (0·4 mole) and dihalide (0·2 mole) in tetrahydrofuran (20 ml) was added. The reaction in general appeared to have an induction period of half to one hour and could be followed by observing the temperature rise and the development of an opacity in solution due to lithium halide production. In these experiments strict temperature control was not used but the temperature was not allowed to exceed 30°C.

The experiments involving butadiene were modified in that after addition of the dihalide to the tetrahydrofuran solution the nitrogen bubbler was turned off and the required volume of butadiene distilled into the reaction vessel which was then sealed for the remainder of the reaction.

In some experiments an electron acceptor such as naphthalene or tetraphenylethylene was added to the system to give a lithium salt. This serves three functions. First, the salt produced scavenges the solution of residual adventitious impurities, secondly, it initiates the formation of the dimeric dianion by electron transfer and finally, it indicates the end of the polymerization by redeveloping the characteristic colour of the lithium salt..

The polymeric materials were isolated in a number of ways, but whereever possible by precipitation in a large excess of methanol. Invariably the solids were redissolved and the precipitation procedure repeated before drying in a rotary evaporator. The separated butadiene and isoprene copolymers were mostly white emulsions which, when redissolved in tetrahydrofuran and the liquid removed in a rotary evaporator, became straw coloured, highly viscous clear liquids.

CHARACTERIZATION

The 60 MHz n.m.r. spectra were measured in carbon disulphide or carbon tetrachloride solutions using a Perkin–Elmer R10 spectrometer. Infra-red analyses were produced on a Perkin–Elmer 337 spectrometer.

The specific viscosities of 1% w/v solutions of the polymers in tetrahydrofuran were determined at 25°C for a measure of the chain length achieved.

RESULTS AND DISCUSSION

The experimental details, viscosities, and the aliphatic to aromatic hydrogen ratios obtained from the peak areas of the n.m.r. spectra of a representative selection of the polymers synthesized are summarized for vinyl monomers in *Table 1* and for diene monomers in *Table 2*. A detailed discussion of the n.m.r. spectra and some associated infra-red spectra is given in the following paper[4].

In general the yields of copolymer with vinyl monomers are virtually quantitative, but to date those with the dienes are only about 50 to 60 per cent. Attempts to improve the polydiene yields, by adding elecron transfer agents for example, are continuing.

The specific viscosities of the copolymers seem to fall into three categories, the butadiene copolymers having the highest (av. $\eta_{sp} > 0{\cdot}2$), followed by the vinyl copolymers (av. $\eta_{sp} > 0{\cdot}1$) with the copolymers of isoprene being quite low (av. $\eta_{sp} < 0{\cdot}1$). The syntheses were, however, conducted under simple practical conditions principally to determine the validity of the technique and the breadth of its applicability. Experiments are at present in progress to increase the chain length by varying reaction temperature, solvent, alkali metal etc. Materials are also being subjected to more rigorous purification processes although there remains the possibility that the procedure has its own built-in chain stopping reaction. For example, the monomeric radical anions first formed could react with the dihalide to a limited degree instead of dimerizing, thus producing a monohalide radical which, by hydrogen abstraction from solvent, would give a chain stopping monohalide,

$$\text{i.e. } \overline{\mathrm{M}}\mathrm{Li}^{+} + \mathrm{XRX} \longrightarrow \mathrm{M} + \mathrm{LiBr} + {\cdot}\mathrm{RX} \xrightarrow{\mathrm{HS}} \mathrm{HRX} + \mathrm{S}{\cdot}.$$

The aliphatic to aromatic hydrogen ratios listed in the tables are, with two exceptions, in close agreement with those expected from polymers with the repeat unit —[M—R—M]—. The exceptions are both where dibromoethane is used as a linking agent (Runs 2 and 12), and the ratios are significantly too low. We have found this to occur with all other vicinal dihalides so far studied[5] and have shown that they react by an elimination reaction with production of head to head polymer and olefin. The general agreement obtained, however, with all other dihalides shows that the linking reaction proceeds sufficiently quickly to prevent significant amounts of oligomers higher than dimer from being produced. This conclusion is further supported by analysis of the infra-red spectra[4], and by synthesis of the corresponding model compounds prepared by reaction of the monomer with the equivalent monohalide. Although undetectable spectroscopically, the formation of small amounts of trimer and higher oligomers increases the molar ratios of monomer to dihalide required for complete reaction. Thus, for high molecular weight products, the extent of oligomer formation has to be determined and allowed for.

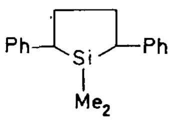
Most of the experiments have been conducted using dibromides although the reactions also proceed smoothly with dichlorides. The diiodides are thought capable of reacting directly with the metal to a significant extent during the time scale of the reaction.

Some attempts have been made to use aromatic dihalides as linking agents with only limited success. It is suspected that side reactions occur which involve the formation of benzyne intermediates[6].

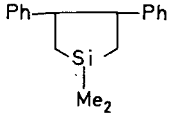
The effect of the nature of the linking agent on the physical properties of the final polymer is illustrated in *Table 2* by isoprene and butadiene. When a purely aliphatic linking agent is used, the product is a highly viscous straw coloured oil. Introduction of aromatic groups into the polymer backbone by using *p*-xylylene dibromide, or as pendant groups by using diphenyldichloromethane, gives polymers which are rubbery solids.

Qualitative spectroscopic analysis of the diene copolymers indicates that the diene is incorporated predominantly by 1,2 (or 3,4) addition and a more detailed structural analysis is in progress. Some experiments have been carried out on crosslinking of the diene polymers and give rubbery materials.

When geminal dihalides are used as linking agents, there is a possibility of cyclization reactions occurring to form cyclopentane derivatives, and we have reported the isolation and identification of a number of these[7]. Weyenberg *et al.*[8] have also reported the formation of silacyclopentane derivatives when styrene reacts with dimethyl dichlorosilane and lithium in tetrahydrofuran. They observed that with a 1 : 1 monomer to silane molar ratio they got a 71 per cent yield of compound (I) whereas under identical conditions but with a molar ratio of 2 : 1 they obtained compound (II) in 75 per cent yield as the sole product.



I



II

We have carried out similar experiments with the same result. The formation of (I) is readily explained by a direct reaction of the dimer dianion with one molecule of the silane. The formation of (II) presents greater difficulty, and Weyenberg *et al.* suggest a completely different mechanism involving the formation of a transient silacyclopropane. We favour the following reaction scheme where the monomer radical anion is additively attacked by the silane before dimerization can occur because of the higher silane concentration, i.e.

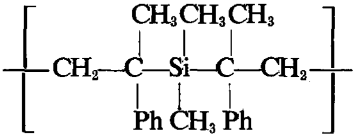
$$\mathrm{(CH_3)_2\,SiCl_2 + CH_2\overset{\cdot\cdot}{-}CHPh^{-}Li^{+} \longrightarrow \underset{A}{(CH_3)_2\,SiClCH_2—CHPh^{\bullet}} + LiCl}$$

$$\mathrm{A + CH_2\overset{\cdot\cdot}{-}Ph^{-}Li^{+} \longrightarrow \underset{B}{{}^{\bullet}PhHC—CH_2—Si\,(—CH_3)_2—CH_2—CHPh^{\bullet}} + LiCl}$$

followed by radical coupling of B to give product (II).

Whatever the mechanism, however, it is still strange that two distinct major products are obtained by merely changing the concentration of one ingredient by a factor of two.

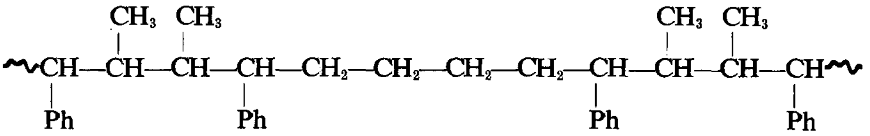
The nature of the monomer used also affects the products greatly. α-Methylstyrene reacted with dimethyldichlorosilane at these two concentrations and under the same conditions as styrene gave a polymer in both cases which was shown by n.m.r. analysis to have the repeat unit



$$\left[—CH_2—\underset{Ph}{\overset{CH_3}{C}}—\underset{CH_3}{\overset{CH_3}{Si}}—\underset{Ph}{\overset{CH_3}{C}}—CH_2—\right]$$

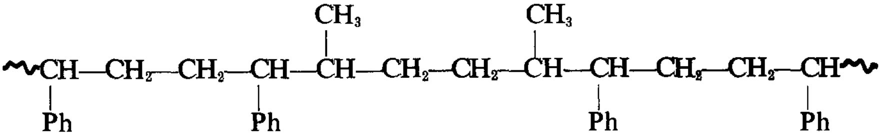
and other inorganic halides such as di(n-butyl)dichlorogermane also react with α-methylstyrene to give polymeric materials of this general formula. Apparently the two extra methyl groups in the α-methylstyrene dimer cause a loss of flexibility in the compound which considerably reduces the probability of cyclization.

When dihalides are used which are neither geminal nor vicinal the side reactions described become negligible and polymers are exclusively produced. These polymers then have closely defined structures which may be systematically varied to determine the effect of these variations on their properties. Two examples of these changes are tabulated. First, the α,ω-dibromides $(CH_2)_nBr_2$, where n has been varied from one to ten, have been reacted with various monomers, thus producing polymers which may be regarded as regular copolymers of methylene and, say, styrene, but with predetermined proportions. Glass transition temperatures of these materials have been shown to vary in a predicted manner between the two extreme homopolymers[9]. Secondly, polymers have been prepared with structures (III) and (IV) by linking β-methylstyrene with 1,4-dibromobutane (run 21) and by linking styrene with 2,5-dibromohexane (run 8).



$$\sim\underset{Ph}{CH}—\overset{CH_3}{CH}—\overset{CH_3}{CH}—\underset{Ph}{CH}—CH_2—CH_2—CH_2—CH_2—\underset{Ph}{CH}—\overset{CH_3}{CH}—\overset{CH_3}{CH}—\underset{Ph}{CH}\sim$$

III

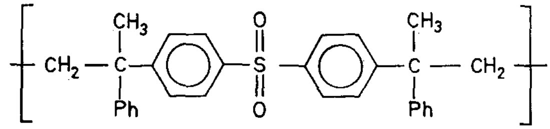


$$\sim\underset{Ph}{CH}-CH_2-CH_2-\underset{Ph}{CH}-\overset{CH_3}{CH}-CH_2-CH_2-\overset{CH_3}{CH}-\underset{Ph}{CH}-CH_2-CH_2-\underset{Ph}{CH}\sim$$

IV

Both these materials may be regarded as being regular 1,1-copolymers of β-methylstyrene and ethylene but with different symmetries. Their ^1H n.m.r. and i.r. spectra are very similar and their physical properties are being tested.

Polar polymers can also be prepared by this method on choice of a suitable dihalide. Thus polysulphones have been prepared by reaction of monomer with p,p'-dichlorodiphenylsulphone giving, with α-methylstyrene, a polysulphone with repeat unit



Although the aliphatic to aromatic hydrogen ratios determined deviate significantly from theory, i.r. measurements indicate a strong absorption due to $—SO_2—$ at 1 160 cm^{-1} and the n.m.r. spectrum shows the characteristic downfield shift of aromatic hydrogens adjacent to the $—SO_2—$ group. The discrepancy in the ratio is probably due to side reactions because an aromatic dihalide was used.

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