Synthesis and Properties of Regular Copolymers II—Spectroscopic Analysis of Regular Copolymers of Vinyl Compounds with Aliphatic Dihalides

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I.r. and n.m.r. spectra of polymers prepared by reacting vinyl monomer with alkali metal in the presence of aliphatic dihalides are discussed and indicate that the materials may be described in general as regular copolymers of repeat unit —[M—R—M]— *where* M *is monomer and* R *is the ligand of the dihalide. The spectra of those polymers prepared with vicinal dihalides, however, confirm that head–head homopolymer is prepared by an elimination reaction. The chemical shifts of a number of such polymers are listed and assigned, and the correlation of these assignments with the polymeric structures is discussed.*

PART I[1] describes the synthesis of a new class of polymers produced by reacting a vinyl or diene monomer with an alkali metal in tetrahydrofuran in the presence of an aliphatic dihalide. These copolymers were ascribed the repeat unit —[M—R—M]—, where M is the monomer and R is the ligand of the dihalide. This assignment was made principally on the basis of ^{1}H n.m.r. analysis where the aliphatic to aromatic hydrogen ratios were determined wherever possible and shown to be in agreement with those calculated for the proposed structure. A more detailed spectroscopic analysis has been carried out to confirm the regularity of the structure and to determine the spectral changes which occur when the polymer composition is systematically varied.

This paper deals with the i.r. and n.m.r. spectra of some of the polymers produced by the reaction of vinyl compounds with aliphatic dihalides. The regular diene copolymers require a more complicated analysis and this is being presented separately in a later communication.

EXPERIMENTAL

Infra-red spectroscopy

Infra-red measurements were carried out on a Perkin–Elmer 337 grating spectrophotometer. Quantitative analyses were determined with carbon tetrachloride as solvent.

Nuclear magnetic resonance spectroscopy

^{1}H n.m.r. spectra were obtained using a Perkin–Elmer R10 60 MHz spectrometer. Solutions in carbon disulphide or carbon tetrachloride were used and chemical shifts measured with respect to tetramethylsilane as internal standard. An associated Digiac computer enabled accumulated spectra to be produced for more accurate analysis.

RESULTS AND DISCUSSION

Seven polymers of the proposed repeat unit $-[CH_2-CHPh-(CH_2)_n-CHPh-CH_2]-$, with n being changed systematically from 1 to 6 and 10, were dissolved in carbon tetrachloride and their infra-red spectra recorded at three different solution concentrations. Peak heights were measured at 1 500, 2 925 and 3 025 cm^{-1} (representing $C{=}C$ skeletal in-plane vibrations, CH_2 stretching and $={C}-H$ stretching frequencies respectively), and the absorbances were shown to obey Beer's law. The absorbances were then corrected for the changing aromatic and aliphatic content of the polymers as predicted by the repeat unit above, and the results compared. The logarithms of these relative extinction coefficients are given in *Figure 1* as a function of n.

It can be seen that the relative extinction coefficients of the two aromatic absorptions remain constant and independent of the value of n. Similarly, the relative extinction coefficients for the aliphatic absorption are also constant except for a significant drop at $n=2$. Thus, except at $n=2$, this constancy supports the assumption of $-[CH_2-CHPh-(CH_2)_n-CHPh-CH_2]-$ as being the repeat unit. This discrepancy at $n=2$ parallels the differences from theory observed in n.m.r. spectra whenever vicinal dihalides have been used as linking agents[2]. In all these cases the aliphatic to aromatic hydrogen ratios exhibit a constancy independent of the nature of the dihalide for a variety of substituted dihalides with a value for the ratio being very close to that of the homopolymer. These results have been interpreted as indicating that a head–head linked homopolymer is formed with elimination of the vicinal dihalide as the equivalent olefin.

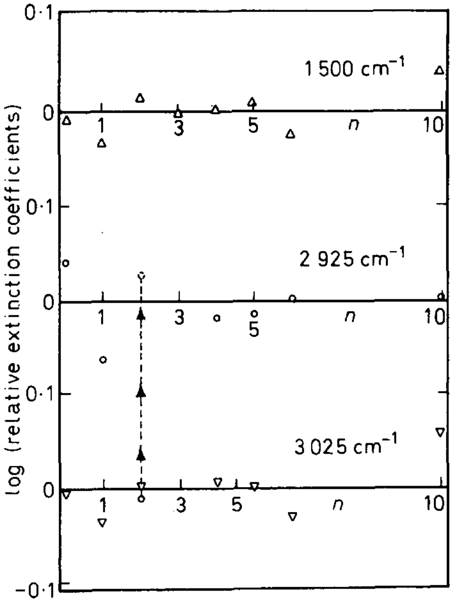


Figure 1—Plot of log (relative extinction coefficients) versus n at three wavelengths for the polymers $[CH_2-CHPh-(CH_2)_n-CHPh-CH_2]_m$

The relative extinction coefficients obtained for $n=2$ were therefore adjusted on this assumption and the new values are also shown in *Figure 1*. The values for the two aromatic absorbances are little changed and their independence of n is maintained. The correction factor for the aliphatic relative extinction coefficient is large and its application brings the relative value at $n=2$ very close to those obtained at the other values of n. Thus the elimination reaction involving vicinal dihalides to produce head-head homopolymer, proposed above, is supported by quantitative analysis of the infra-red spectra.

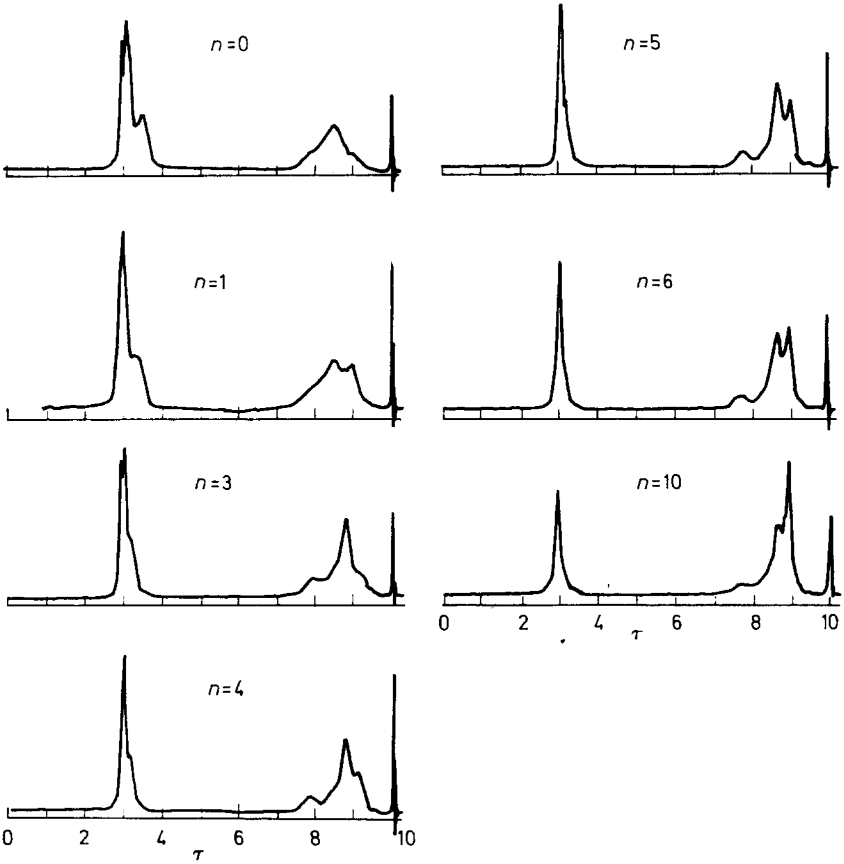


Figure 2—Accumulated ^{1}H n.m.r. spectra of polymers with the repeat unit $\lbrace CH_2—CHPh—(CH_2)_n—CHPh—CH_2 \rbrace$

Accumulated ^{1}H n.m.r. spectra of polymers with the proposed repeat unit $\lbrace CH_2—CHPh—(CH_2)_n—CHPh—CH_2 \rbrace$ are shown in *Figure 2*. Summaries of the chemical shift of peaks in the spectra of these and other compounds are listed and assigned wherever possible in *Tables 1* and *2*. The assignments are given as bracketed numbers after the chemical shifts listed in these tables and refer to the numbers given to the overall assign-

Table 1. Proton chemical shifts (expressed in p.p.m. TMS=10·0) of regular copolymers of styrene and of α-methylstyrene

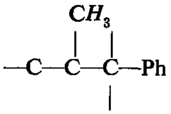
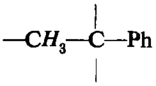
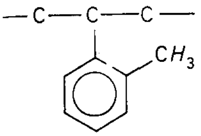
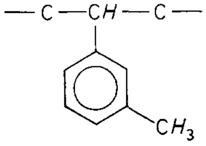
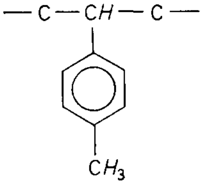
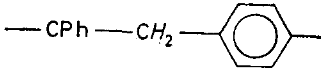
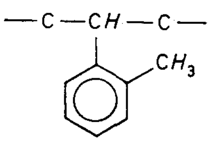
Monomer	*Styrene*		*α-Methylstyrene*	
**Dihalide*	*Aliphatic*	*Aromatic*	*Aliphatic*	*Aromatic*
$\cdot CH_2 \cdot$	8·9 (5) 8·4 (7) 7·9 (11)	3·3 3·0	9·0 (2,4) 8·1 (8)	2·90
$\cdot (CH_2)_2 \cdot$	9·0 (5) 8·5 (5) 7·7 (11)	3·4 3·0	9·4 (2) 9·1 (2) 8·9 (4)	2·90
$\cdot (CH_2)_3 \cdot$	9·1 (3) 8·75 (5) 8·05 (11)	3·2 2·95	9·05 (2) 8·9 (3,4)	2·95
$\cdot (CH_2)_4 \cdot$	9·0 (3) 8·7 (5) 7·8 (11)	3·13 3·0	9·1 (2) 8·95 (3,4)	2·95
$\cdot (CH_2)_5 \cdot$	9·05 (3) 8·7 (5) 7·8 (11)	3·0	9·1 (2) 8·9 (3,4)	2·95
$\cdot (CH_2)_6 \cdot$	9·0 (3) 8·7 (5) 7·75 (11)	2·95	9·05 (2) 8·9 (3,4)	2·95
$\cdot (CH_2)_{10} \cdot$	8·9 (3) 8·6 (5) 7·7 (11)	3·0	8·9 (2) 8·8 (3,4)	2·90
o-$\cdot CH_2C_6H_4CH_2 \cdot$	8·5 (5) 7·45 (14)	3·3, 3·15 3·05, 2·95 2·85	9·0 (2) 8·8 (4) 7·5 (14)	3·0
p-$\cdot CH_2C_6H_4CH_2 \cdot$	8·65 (5) 7·35 (14)	3·4, 3·25 3·1, 3·0	8·95 (2,4) 7·4 (14)	3·8 3·0
$\cdot CH(CH_3)(CH_2)_2(CH_3)CH \cdot$	9·4 (1) 8·6 (5) 7·8 (11)	3·0	9·5 (1) 9·0 (2) 8·5 (3,4)	2·95

*Of form X—R—X where R is the ligand shown.

Table 2. Proton chemical shifts (in p.p.m. TMS=10·0) of regular copolymers of various vinyl monomers with dibromobutane

β-methylstyrene		o-*methylstyrene*		m-*methylstyrene*	
Al	Ar	Al	Ar	Al	Ar
9·2 (1) 8·7 (5) 7·8 (11)	3·4 2·9	9·0 (3), 8·7 (5) 7·85 (10) 7·35 (15)	3·0	9·0 (3) 8·7 (5) 7·75 (12)	3·2 3·1
p-*methylstyrene*		*1,1-diphenylethylene*		*4-vinyldiphenvl*	
Al	Ar	Al	Ar	Al	Ar
9·0 (3) 8·75 (5) 7·7 (13)	3·3 3·1	9·4 (3), 9·2 (3) 8·45 (6), 8·3 (9) 8·2	3·0 2·95 2·90	8·8 (3) 8·6 (5) 7·7 (11)	3·1, 2·9 2·7, 2·6 2·5

Table 3. Assignment of aliphatic peaks in ^1H n.m.r. spectra of regular copolymers

No.	*Average* τ	*No. of readings*	*Standard deviation*	*Assignment*
1	9·37	3	0·17	 $-C-\overset{|}{C}-\overset{CH_3}{\underset{|}{C}}-Ph$
2	9·09	12	0·11	 $-CH_3-\overset{|}{\underset{|}{C}}-Ph$
3	9·00	15	0·08	$-C-CH_2-C-$
4	8·87	11	0·11	$-C-CH_2-C(CH_3)-Ph-$
5	8·70	15	0·09	$-C-CH_2-CHPh-$
6	8·45	1	—	$-CPh_2-CH_2-CH_2-CH_2-$
7	8·40	1	—	$-PhCH-CH_2-CHPh-$
8	8·30	2	0·30	$-PhC(CH_3)-CH_2-C(CH_3)Ph$
9	8·30	1	—	$-CPh_2-CH_2-CH_2-CPh_2-$
10	7·85	1	—	
11	7·80	10	0·11	$-C-CHPh-C-$
12	7·75	1	—	
13	7·70	1	—	
14	7·47	4	0·15	
15	7·35	1	—	

ments in *Table 3*. *Table 4* gives the relative areas of various distinct and assigned absorptions and these are compared with the values calculated on the basis of the —[M—R—M]— repeat unit. The aliphatic to aromatic hydrogen ratios have been given previously in Part I[1] and are therefore not included in this table.

The spectra in *Figure 2* show a number of features which vary as a function of n. In the aromatic region starting at $n=0$ (assuming the elimination reaction with vicinal dihalides results in head to head styrene homopolymer) the minor aromatic peak at $3{\cdot}3\tau$ moves downfield with increasing n, being observable only as a shoulder of the main peak for $n=4$ and a sharpening of the main peak at $3{\cdot}0\tau$ for higher values of n. Two peaks at 3·0 and $3{\cdot}4\tau$ were observed in the aromatic region of head to tail polystyrene by Bovey *et al.*[3], the former being ascribed to the meta- and para-hydrogens and the latter to the ortho-hydrogens. The resolution of the two peaks corresponds to that observed by Bovey for atactic polystyrene rather than isotactic. The high-field shift of the ortho protons arises as a result of increased shielding experienced when the planes of adjacent phenyl groups are orthogonal. The ortho protons of one ring then lie above the centre of the π-electron clouds of neighbouring rings and the diamagnetic field induced by the ring current gives rise to a shift to high field[4]. In the copolymers, the phenyl group is separated from its two neighbouring phenyls by 4 and $n+2$ carbon atoms. The persistence of a high-field shift up to $n=4$ (separation by six carbon atoms) indicates that it exists when the carbon atoms are separated by four carbon atoms (i.e. in the tail to tail dimer units), but its disappearance at higher values of n means that the ortho protons must experience an environment which is an average of the effects of the two immediate neighbouring phenyl groups distant by 4 and $n+2$ carbon atoms respectively. This is borne out by the non-persistence of the high-field shift. Thus, assuming the repeat unit —[M—R—M]— from other evidence, this indicates that there is free rotation about the carbon–phenyl bond, in agreement with Bovey's deduction for head to tail polystyrene[3]. The α-methylstyrene copolymers do not show two aromatic peaks, presumably due to steric hindrance by the methyl groups[5] preventing the ortho protons from adopting the highly shielded positions above the phenyl rings.

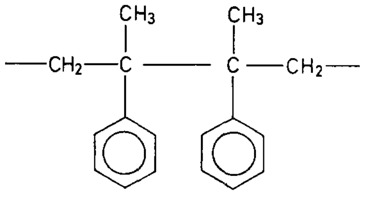
In the aliphatic region of the spectra shown in *Figure 2*, a peak appears at $9{\cdot}0\tau$ when $n=3$, as expected, and grows in intensity with increasing n. This, together with the areas of the aliphatic peaks relative to the aromatic peaks (*Table 4*), allows the following assignments to be made: $9{\cdot}0\tau$: $—CH_2—\mathit{CH}_2—CH_2—$, $8{\cdot}7\tau$: $—CH_2—\mathit{CH}_2—CHPh—$ and $7{\cdot}8\tau$: $—CH_2—\mathit{CH}Ph—$. These values are in agreement with chemical shift data for equivalent small molecules. A peak at $8{\cdot}4\tau$ appears only for $n=1$ and may therefore be assigned to the grouping $—CHPh—\mathit{CH}_2—CHPh—$ as in head to tail polystyrene[3].

The observation of two separate resonances at 9·4 and $9{\cdot}1\tau$ assigned to methyl protons in the polymer produced by the reaction between α-methylstyrene and dibromoethane is due to the presence of different tacticities. As this material is assumed to be head to head poly(α-methylstyrene), it can be seen that in the two possible configurations indicated below, configura-

Table 4. ^{1}H area ratios of regular copolymers

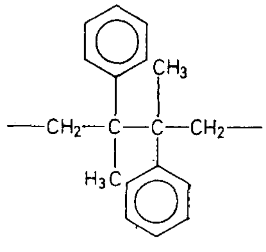
Assignment ratio	*Monomer*	*Dihalide*	*Area ratio*	
			Theory	*Exptl*
$\dfrac{-\mathrm{C}-\mathrm{C}H\mathrm{Ph}-\mathrm{C}-}{\text{Aromatic}}$	styrene	$\cdot(\mathrm{CH_2})_3\cdot$	0·20	0·23
		$\cdot(\mathrm{CH_2})_4\cdot$	0·20	0·25
		$\cdot(\mathrm{CH_2})_5\cdot$	0·20	0·18
		$\cdot(\mathrm{CH_2})_6\cdot$	0·20	0·21
		$\cdot(\mathrm{CH_2})_{10}\cdot$	0·20	0·21
	o-methylstyrene	$\cdot(\mathrm{CH_2})_4\cdot$	0·25	0·28
$\dfrac{-\mathrm{CH_2}-\mathrm{C}H_2-\mathrm{CH_2}-}{-\mathrm{CH_2}-\mathrm{C}H_2-\mathrm{CHPh}-}$	styrene	$\cdot(\mathrm{CH_2})_4\cdot$	0·50	0·62
		$\cdot(\mathrm{CH_2})_5\cdot$	0·75	0·80
		$\cdot(\mathrm{CH_2})_6\cdot$	1·0	1·16
		$\cdot(\mathrm{CH_2})_{10}\cdot$	2·0	2·2
$\dfrac{-\mathrm{C}H\mathrm{Ph}-\mathrm{C}H_2-\mathrm{Ph}-}{\text{Aromatic}}$	styrene	*o*-$\cdot\mathrm{CH_2C_6H_4CH_2}\cdot$	0·43	0·40
		p-$\cdot\mathrm{CH_2C_6H_4CH_2}\cdot$	0·43	0·40
$\dfrac{-\mathrm{C(CH_3)Ph}-\mathrm{C}H_2-\mathrm{Ph}-}{\text{Aromatic}}$	α-methylstyrene	*o*-$\cdot\mathrm{CH_2C_6H_4CH_2}\cdot$	0·29	0·32
		p-$\cdot\mathrm{CH_2C_6H_4CH_2}\cdot$	0·29	0·31
$\dfrac{-\mathrm{C(CH_3)Ph}-\mathrm{C}H_2-\mathrm{C(CH_3)Ph}-}{\text{Aromatic}}$	α-methylstyrene	$\cdot\mathrm{CH_2}\cdot$	0·20	0·21
$\dfrac{\beta\text{-}\mathrm{CH_3}}{\text{Aromatic}}$	styrene	$\cdot\mathrm{CH(CH_3)(CH_2)_2(CH_3)CH}\cdot$	0·60	0·57
	α-methylstyrene	$\cdot\mathrm{CH(CH_3)(CH_2)_2(CH_3)CH}\cdot$	0·60	0·57
	β-methylstyrene	$\cdot(\mathrm{CH_2})_4\cdot$	0·60	0·63
$\dfrac{o\text{-}\mathrm{CH_3}}{\text{Aromatic}}$	*o*-methylstyrene	$\cdot(\mathrm{CH_2})_4\cdot$	0·75	0·81
$\dfrac{m\text{- or }p\text{-}\mathrm{CH_3}+\text{3ary H}}{\text{Aromatic}}$	*m*-methylstyrene	$\cdot(\mathrm{CH_2})_4\cdot$	1·0	1·04
	p-methylstyrene	$\cdot(\mathrm{CH_2})_4\cdot$	1·0	1·03
$\dfrac{-\mathrm{C}H_2-\mathrm{C(Ph)_2}-\mathrm{C}H_2}{\text{Aromatic}}$	1,1-diphenylethylene	$\cdot(\mathrm{CH_2})_4\cdot$	0·40	0·42

tion (b), where the methyls lie above the centre of the phenyl rings, leads to greater shielding of the methyl group and consequently has been assigned to the higher field shift.



(a)

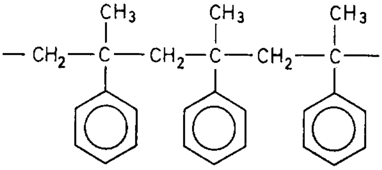
$\tau = 9{\cdot}1$



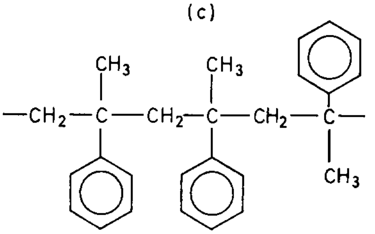
(b)

$\tau = 9{\cdot}4$

This is in accordance with the n.m.r. spectrum of head to tail poly-(α-methylstyrene)[6] where three methyl resonances at 9·21, 9·74 and 10·08τ are observed due to the following configurations respectively:

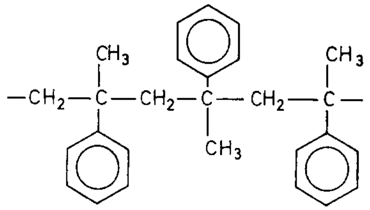


(c)



(d)

and



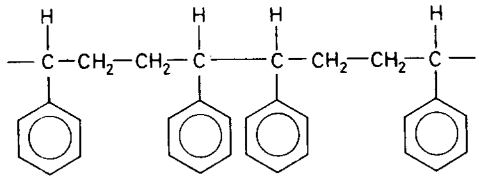
(e)

When the methyls are separated by four or more carbon atoms there is no observable effect, and in the head to head homopolymer, the configuration where a methyl group is sandwiched between two phenyl groups, leading to the very high field shift of 10·08τ, cannot occur. Molecular models indicate that a similar situation does not arise in head to tail polystyrene because the α-protons do not lie over the centre of the phenyl groups due to their smaller size.

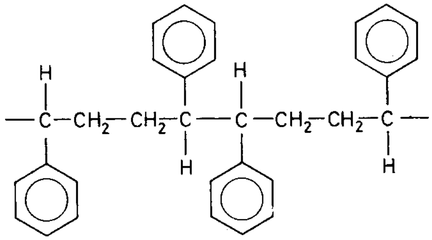
In head to head polystyrene (from the styrene–dibromoethane reaction) it must be assumed that the inductive effect of two adjacent phenyl groups is sufficient to bring the methylene absorption down to 8·5τ (cf. 8·7τ for higher values of n) and that the shoulder at 9·0τ is due to increased shielding by the phenyl in the manner discussed above in configuration (f) as opposed to (g).

For all other values of n the phenyl groups are separated by three or more carbon atoms and different tacticities do not give rise to different absorptions.

The spectra of the regular copolymers of β-methylstyrene with α,ω-dibromo-n-butane and styrene with 2,5-dibromohexane show little real difference. These polymers can both be regarded as regular 1,1 copoly-



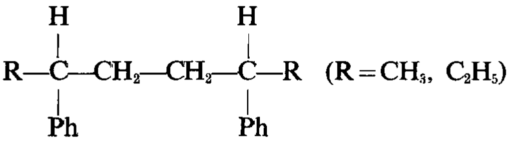
(f)



(g)

mers of β-methylstyrene and ethylene with different symmetries. The peak assignments for the former are 9·2τ: $-\mathrm{CH}_3$, $-\mathit{CH}_2-\overset{|}{\mathrm{C}}\mathrm{HCH}_3-$, 8·7τ: $-\mathit{CH}_2-\mathrm{CHPh}-$, 7·8τ: $-\mathit{CH}\mathrm{CH}_3-$, $-\mathit{CH}\mathrm{Ph}-$; and for the latter are 9·4τ: $-\mathrm{CH}_3, -\mathit{CH}_2-\overset{|}{\mathrm{C}}\mathrm{HCH}_3-$, 8·6τ: $-\mathit{CH}_2-\mathrm{CHPh}-$, 7·8τ: $-\mathit{CH}\mathrm{CH}_3$, $-\mathit{CH}\mathrm{Ph}$. Assuming from molecular models that the shielding of the methyls by the phenyl ring currents is much the same in both structures, the methyl-methylene shift to lower fields in the former polymer must be due to the larger inductive effect of the two close phenyl groups in contrast to that of the solitary close phenyl in the styrene copolymer.

Some interesting points arise in the three copolymers of *o*-, *m*- and *p*-methylstyrene with α,ω-dibromo-*n*-butane in which the methyl protons absorb at 7·85τ, 7·75τ and 7·70τ respectively. The up-field absorption of the ortho-methyl group is due to the greater shielding of the methyl in this position by the ring current of the nearest phenyl group than in the other two cases due to the geometry of the system. A much larger effect is observed with the methine proton absorptions in these three copolymers, due to a similar cause. The methine protons absorb at 7·35τ, 7·75τ and 7·70τ respectively for the *o*-, *m*- and *p*-methylstyrenes and at 7·80τ for the equivalent unsubstituted styrene copolymer. The anomalous down-field shift in the ortho-substituted case suggests steric hindrance as the cause. The shielding of the methine protons by the ring current of the adjacent phenyl which can occur in the other copolymers is minimized in this case by the presence of the ortho-methyl, resulting in the up-field shift of the *o*-methyl hydrogen absorption and the much larger down-field shift of the methine hydrogen peak. This view is supported by consideration of model compounds. The chemical shift of the methine hydrogen in cumene, where shielding cannot occur, is at 7·2τ and corresponds more closely to the peak for the ortho-substituted copolymer. The methine absorptions in the compounds



$$R-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}-CH_2-CH_2-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle Ph}{|}}{C}}-R \quad (R = CH_3,\ C_2H_5)$$

where methine–phenyl interaction can occur is significantly up-field at 7·55τ. Finally, in the compound 1,4-diphenylcyclohexane, where the methine–phenyl separation is the same as in the 1,4-dialkyl-1,4-diphenylbutanes, the methine absorption is again down-field at 7·3τ. In this case the groups are rigidly held and cannot adopt the highly shielded position.

Wherever the aliphatic peaks are reasonably well resolved, their areas relative to other identified peaks, usually aromatic, have been determined, *Table 4*, and compared with those predicted by the repeat unit —[M—R—M—]—. The very good agreements obtained in *Table 4* and in the table in Part I, together with the trends discussed above, confirm the repeat unit —[M—R—M—]— to predominate in all the polymers except those prepared with vicinal dihalides.

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