Determination of the structure of polyethylarylmethylenes by ^{13}C nuclear magnetic resonance spectroscopy

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Ethyl-substituted polyarylmethylenes have been prepared by reacting ethylbenzene with bis(chloromethyl)benzene (BCMB) under Friedel–Crafts conditions. The nature of the substitution patterns in the aromatic rings has been established using ^{13}C Fourier transform nuclear magnetic resonance spectroscopy. The ethyl groups can be used to distinguish between those benzene rings derived from ethylbenzene and those from BCMB and can thus facilitate an understanding of polymerization mechanisms. The structure of the products consists of di-, tri- and tetra-substituted benzene rings. Penta-, hexa- and *meta* di-substituted rings appear to be excluded. No chloromethyl groups could be confirmed.

(Keywords: ^{13}C nuclear magnetic resonance; Friedel–Crafts; polymer structure; aromatic; substitution)

INTRODUCTION

The synthesis and properties of polyarylenemethylenes (PAMs) have been reported in the literature by several authors[1–8]. However, their practical application has been largely unsuccessful. One view is that this can be attributed to the brittle nature of the crosslinked products and that this, in turn, is related to their highly branched structure. Attempts to produce linear polymers have been hindered by the inadequacy of established methods of determining structures. Recently, structural characterizations have been attempted by infra-red spectroscopy[1] and by ^{1}H *FT* n.m.r.[9] but overlapping of numerous absorptions has caused difficulty. These overlapping absorptions are a consequence of the large number of substitution patterns in the aromatic rings of the highly branched polymer chains.

A more thorough structural analysis of a PAM has been performed recently by Hasan and Tsonis[10], using ^{13}C *FT* n.m.r. They chose a polybenzyl formed by the self-condensation of benzyl chloride and concluded that the only aromatic substitution patterns present were:

(i) mono-substituted end groups,
(ii) *o* and *p* di-substituted rings,
(iii) 1,2,4-tri-substituted rings,
(iv) 1,2,4,5-tetra-substituted rings.

The bulk of the product consisted of (iii). All other substitution patterns, such as *meta* di-substituted rings and penta- and hexa-substituted rings, were thought to be absent.

However, the broad and overlapping nature of the resonances in the spectra presented raises some questions and it is difficult to be sure that there are no *meta* di-substitution or tri-substitution patterns.

This paper presents the results of a structural analysis by ^{13}C *FT* n.m.r. of a similar PAM, produced by the reaction of ethylbenzene with bis(chloromethyl)benzene (BCMB). The polymeric product contains ethyl side chains and, if no branching occurred, it would be expected to have the linear structure shown in *Figure 1*. Since the ethyl group distinguishes one benzene ring from the other involved in the condensation reaction, it is possible to deduce a mechanism for the reaction. Moreover, the spectra obtained from such a polymer are much better resolved than is the case with polybenzyl.

EXPERIMENTAL

Ethyl-substituted polybenzyl was prepared as follows. Two moles (350 g) of BCMB and 6.4 moles (678 g) of ethylbenzene were stirred under nitrogen in a 5 dm^3 glass reaction vessel fitted with a reflux condenser. The temperature was raised to 100°C and 2.0 cm^3 of 10% v/v stannic(IV) chloride in dichloroethane solution added.

The temperature was raised again to 125°C, at which point hydrogen chloride began to be evolved. This was neutralized by passing it through sodium hydroxide solution of known concentration. Further stannic chloride additions were made whenever the hydrogen chloride evolution slowed down, until it was calculated that sufficient had been evolved to account for all the BCMB. The resulting viscous reaction mixture was diluted with ethylbenzene and extracted three times with aqueous hydrogen chloride solution, before drying over anhydrous sodium sulphate. The volume was then reduced to a minimum using a rotary evaporator and the polymer precipitated out three times by dropwise addition to methanol. Residual volatiles were removed by heating under vacuum (down to 2.6×10^{-5} bar) at 100°C. The yield was typically about 450 g, or 0.93 moles of polymer.

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The number-average molecular weight ($\bar{M}_n$) of ethyl-substituted polybenzyl was determined for one sample by means of a Knauer vapour-pressure osmometer and found to be 482.

The ^{13}C *FT* n.m.r. spectrum was obtained using a 10% w/v solution in deuterochloroform, with tetramethylsilane (TMS) as internal standard. d-Chloroform was used as the internal field-frequency lock signal. The proton-decoupled spectra were run on a Brucker WP80 instrument at 20.15 MHz, with 16 000 data points. Pulse width was 6 μs, the relaxation delay was 4.00 s and the number of transients was 11 312.

RESULTS AND DISCUSSION

Additive parameters

Figure 2 shows the proton-decoupled ^{13}C *FT* spectrum of the ethyl-substituted polybenzyl. *Table 1* divides the spectrum into five distinct regions.

A structural analysis was performed by the method of Hasan and Tsonis[10], using only the absorptions arising from the aromatic regions.

The procedure can be summarized as follows. The theoretical chemical shifts were calculated, for each carbon in the aromatic rings, for all possible substitution patterns, by the summation of additive parameters, derived from the spectra of model compounds, notably benzene and diphenylmethane. The spectral changes occurring when a benzyl group is introduced into a phenyl ring were noted. For example, unsubstituted benzene gives a single absorption at δ128.5, but the addition of a benzyl group gives shifts in absorption of +12.5 ppm for the ring carbon at the substituted position, and *ortho*, *meta* and *para* positions show shifts of +0.3, +0.8 and −2.6 ppm respectively. When polysubstitution takes place the calculated chemical shift at a substituted position has to take into account further additive parameters arising from steric effects. Thus, when a carbon atom is in the *ortho*, *meta* or *para* position relative to a substituent, further additive parameters of −2.0, +0.5 or +0.8 ppm have to be inserted into the calculation of the δ values.

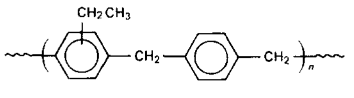


Figure 1 Simplified structure of the ethyl polybenzyl

Ethyl side chains shift the δ value for the substituted position by +15.6 ppm, and for the *o*, *m* and *p* positions by −0.5, 0 and +2.6 ppm, with further steric shifts of −2.0, +0.5 and +0.8 ppm respectively. The effect of the ethyl group is to increase the spread of the aromatic signals by increasing the number of additive parameters and it therefore makes the analysis easier than for a polybenzyl-only chain.

Table 2 shows the calculated chemical shifts for all the possible substitutions in the ethyl polybenzyl. *Table 3* gives the corresponding labelled substitution patterns. Structural analysis was carried out by comparing these values with two expanded aromatic regions of the spectrum, i.e. the unsubstituted region (*Figure 3*) and the substituted region (*Figure 4*). These regions are both very well resolved and individual absorptions differing by only 0.1 ppm can be distinguished.

The following appear to be absent:

(i) penta- and hexa-substitutions, as expected from steric considerations;

Table 1 Regions of absorption in the ^{13}C *FT* spectrum

Structural unit	Chemical shift (ppm)
Ethyl CH_3	14–16
Ethyl CH_2	25–29
Methylene bridge CH_2	38–42
Unsubstituted aromatics	125–132
Substituted aromatics	135–143

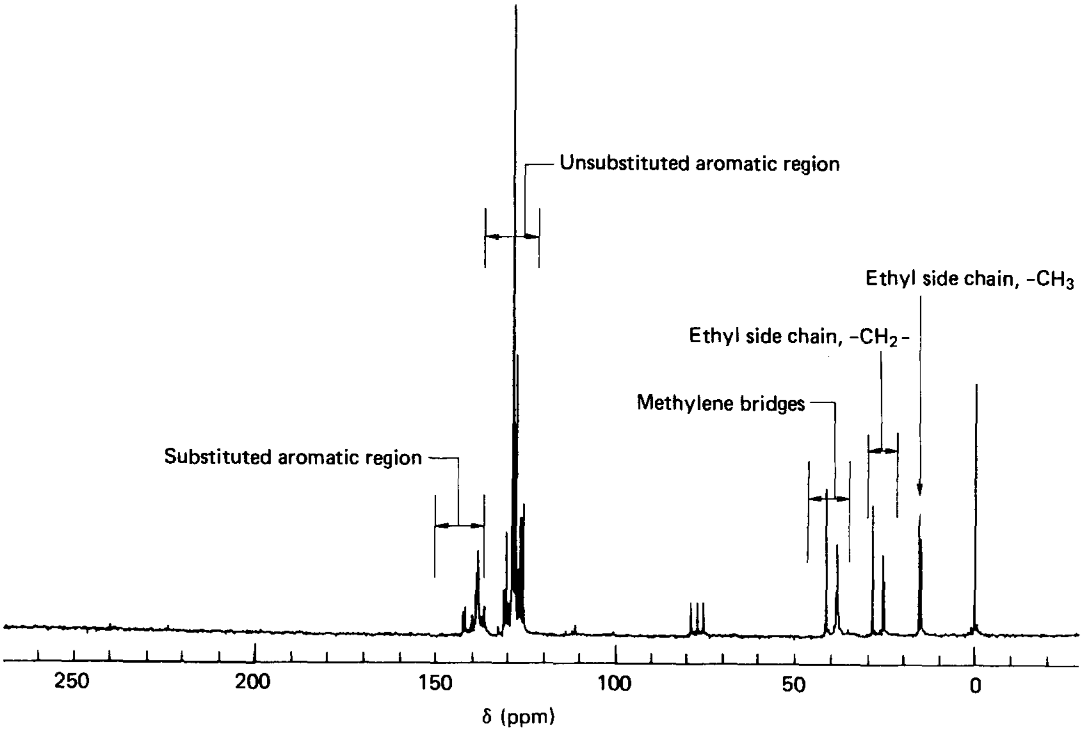


Figure 2 Proton-decoupled ^{13}C *FT* n.m.r. spectrum of the ethyl polybenzyl

Table 2 Calculated ^{13}C chemical shifts for all substitution patterns possible in the ethyl polyarylmethylene

Substitution pattern	Calculated chemical shifts (ppm)					
	C1	C2	C3	C4	C5	C6
I	142.4	138.5	128.8	126.7	131.1	128.8
II	145.4	128.3	131.5	126.2	129.3	131.1
III	142.3	128.8	128.8	141.8	128.8	128.8
IV	139.2	129.6	129.6	139.2	129.6	129.6
V	139.3	139.3	129.6	126.7	126.7	129.6
VI	142.3	129.1	142.3	126.2	126.2	126.2
VII	140.7	139.8	126.2	127.5	126.2	141.8
VIII	143.7	129.5	139.7	127.0	129.6	136.7
IX	140.6	129.6	126.2	140.5	129.1	139.8
X	141.7	136.8	139.8	127.0	126.7	125.7
XI	146.7	125.7	142.8	126.5	142.8	125.7
XII	143.6	129.1	139.8	137.2	129.6	126.2
XIII	140.6	137.6	140.6	127.0	127.5	127.0
XIV	137.5	140.6	129.9	140.5	127.0	130.4
XV	143.6	126.5	143.6	126.5	143.6	126.5
XVI	144.0	138.1	138.0	137.8	127.0	138.0
XVII	138.9	141.1	126.5	141.8	126.5	141.1
XVIII	138.8	138.8	130.7	138.8	138.8	130.7
XIX	138.7	138.9	138.9	138.7	127.8	127.8
XX	141.9	135.8	141.9	127.3	141.8	127.3
XXI	144.7	135.0	141.1	127.3	141.0	136.7
XXII	141.9	138.1	138.1	138.8	127.0	127.0
XXIII	141.9	138.0	129.9	138.8	138.0	129.9
XXIV	144.9	126.5	141.1	135.8	141.1	126.5
XXV	140.1	137.1	140.2	137.1	140.1	128.1
XXVI	143.4	136.3	139.4	137.1	135.9	127.3
XXVII	140.2	139.4	136.3	139.3	127.3	139.3
XXVIII	143.3	136.3	139.3	128.1	139.3	136.3
XXIX	All positions 138.4					
XXX	141.5	137.6	137.6	138.4	137.6	137.6

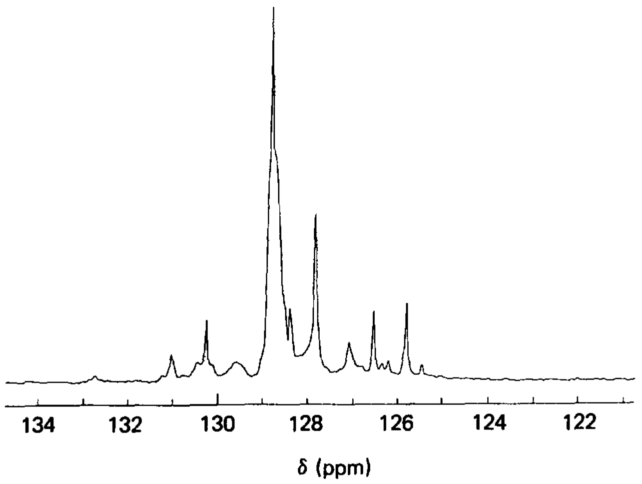


Figure 3 Expanded unsubstituted aromatic region of *Figure 2*

(ii) products that can be formed only via *meta* substitutions (e.g. structures XI, II in *Table 3*)—this suggests that *o* and *p* substitution are strongly favoured;

(iii) products arising from the rearrangement of BCMB units by dealkylation and subsequent realkylation (e.g. structures V, VI in *Table 3*);

(iv) products of the 1,2,3,5-tetrasubstituted type (structures XX and XXI); and

(v) chloromethyl end groups—this is expected, as the second chloromethyl group in BCMB is much more reactive than the first[6].

Taking points (ii) and (iii) together, it can be deduced that the reversible nature of Friedel–Crafts alkylation does not lead to alkylation/dealkylation reactions, and therefore the ethyl side chain acts as a marking label for the ethylbenzene units.

Prevailing substitution pathways

Three possible routes by which tetra-substituted aromatic rings could be formed from an ethylbenzene unit are shown in *Figure 5*, using *ortho* and *para* substitutions in each case. Two routes to tetra-substituted rings from the BCMB unit are shown in *Figure 6*. Combining all the likely di-, tri- and tetra-substituted rings from *Table 3*, we can envisage the final structure of an ethyl polybenzyl, not as a linear molecule such as that shown in *Figure 1*, but as a complex branched chain with many of the features depicted in *Figure 7*. The high degree of branching indicated here is probably undesirable for crosslinkable polymers, where ease of processing and mechanical toughness are required. Synthetic methods should therefore be sought in which linear structures predominate. The success of any such efforts can be measured by the above methods.

CONCLUSIONS

^{13}C n.m.r. studies confirm that ethyl polybenzyl consists of a multitude of di-, tri- and tetra-substituted ring structures but with no *meta* di-substituted rings and none

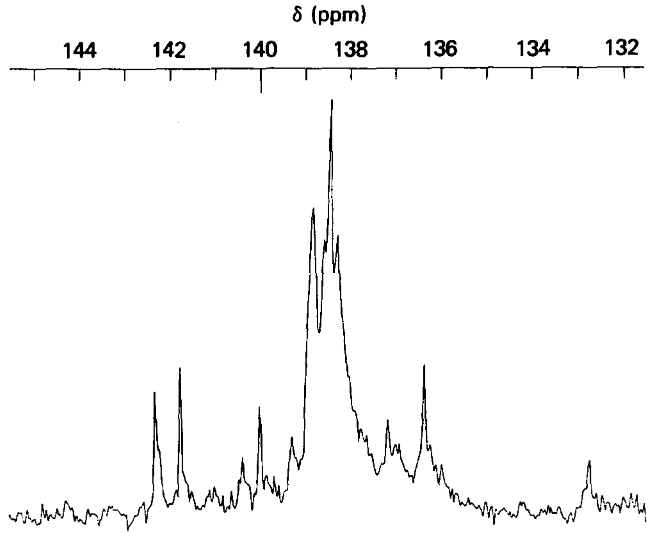


Figure 4 Expanded substituted region of *Figure 2*

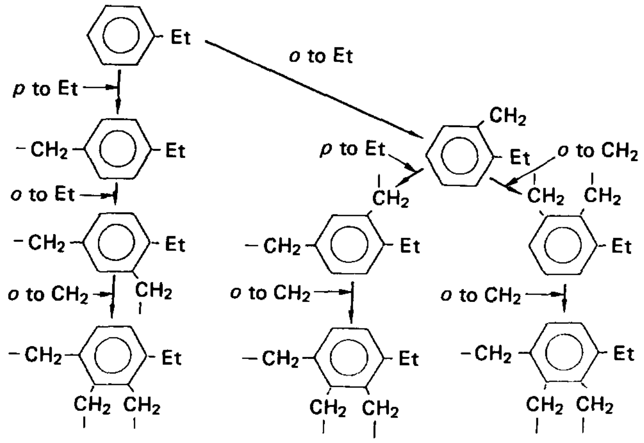
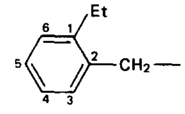


Figure 5 Substitution routes at an ethylbenzene unit

Table 3 Substitution patterns deduced as present or absent

Structures present



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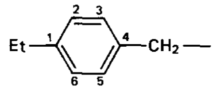

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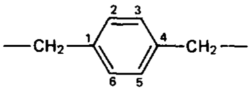

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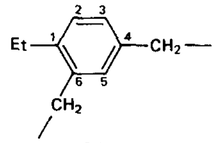

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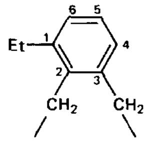

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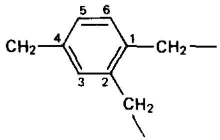

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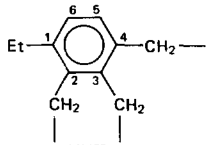

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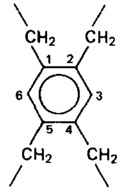

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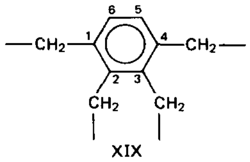
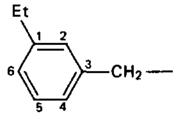


XIX

Structures absent



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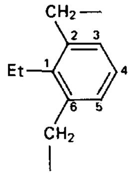

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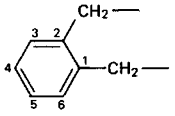

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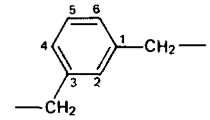
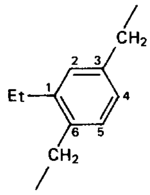


VI

by rearrangement of BCMB



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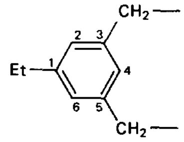

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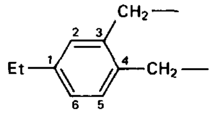

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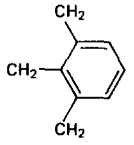

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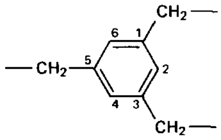

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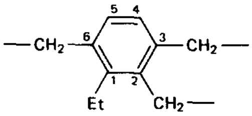

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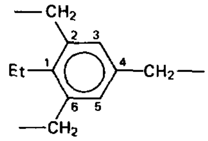

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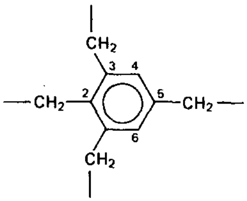

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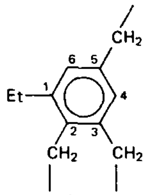

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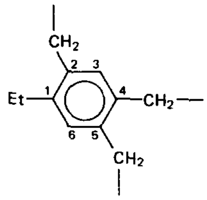

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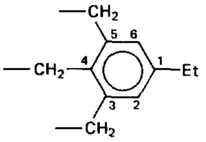

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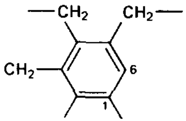

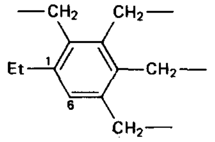

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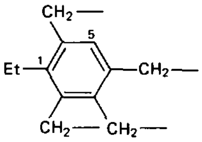

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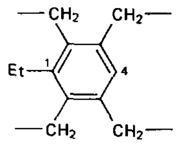

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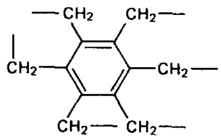

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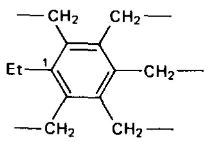

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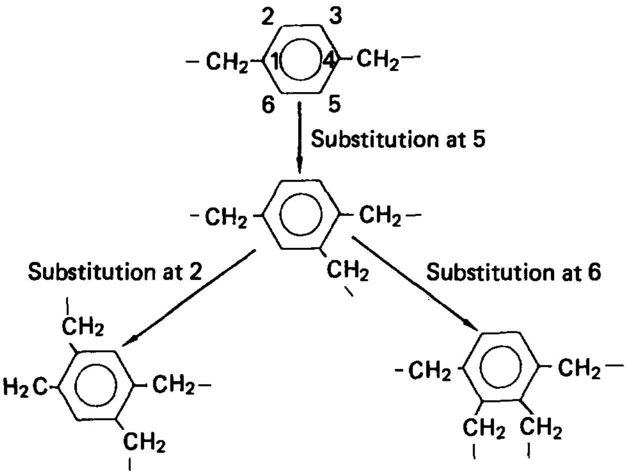

Figure 6 Substitution routes at a BCMB unit

of those poly-substituted structures that could be formed only by *meta* substitution.

Other precluded structures include penta- and hexa-substituted rings and chloromethyl end groups.

Dealkylation/realkylation rearrangements do not take place.

Similar results would be expected with similar monomers, e.g. toluene instead of ethylbenzene. Alkyl-substituted monomers facilitate spectral interpretation and help to elucidate reaction mechanisms.

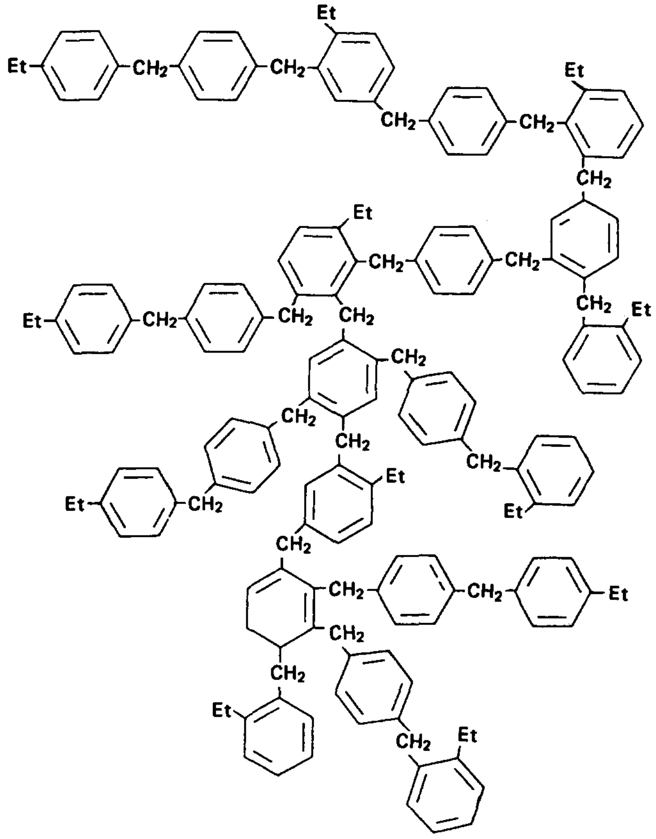

Figure 7 A representative chain of the ethyl polybenzyl

ACKNOWLEDGEMENTS

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