# Poly(alkylbenzyls), a promising new polymeric material

**D. Baudry-Barbier, A. Dormond,*† F. Dumont and F. Duriau-Montagne**

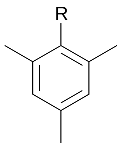
*Laboratoire de Synthèse et d'Electrosynthèse Organométalliques (L.S.E.O.), U.M.R. 5632-C.N.R.S., Université de Bourgogne, 6 bd Gabriel, 21000 Dijon, France*

**The reaction of mesitylene substituted by alkyl or alkoxy chains of various lengths and α,α′-dichloro-*p*-xylene with K10 Montmorillonite as catalyst affords a new class of poly(alkylbenzyls) soluble in common organic solvents.**

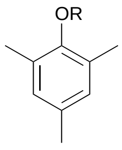
The synthesis of thermostable and water resistant polymers has been widely investigated, but remains even today an important economical challenge. For this purpose, polybenzyls, first reported in 1885,[1] were reinvestigated in the 1970s by several groups.[2–5] These polymers obtained in Friedel–Crafts type polyalkylation reactions[6–8] were found to be thermally stable up to 400 °C,[5,9] but the molecular weights were often very low[5] and little information about their nature and their properties was available. All these materials were described as insoluble in organic solvents, this insolubility preventing any possibility of industrial use. Moreover, it was noted that although *para* substitution in the main chain was predominant,[5,9] the possibility of lateral substitution on the polybenzyl skeleton leading to branched polymers is not excluded.[10] Then, it was interesting to synthesize non-crosslinked, linear polybenzyls, with a high solubility in usual organic solvents.

To obtain a linear and defined material, the polycondensation of *α*,*α*′-dichloro-*p*-xylene on 1,2,4,5-tetramethylbenzene has been performed using K10 Montmorillonite as catalyst. This acidic clay is widely used as a Friedel–Crafts alkylation and acylation supported catalyst.[11–13] The alkylation is then expected to occur preferentially at the two *para* positions of durene[14] rather than on the disubstituted ring. A linear polymer (**P1**) was effectively obtained: the $^1$H NMR spectrum showed only one singlet due to the four protons of the methylene groups and only one sharp signal due to the four protons of the equivalent aromatic protons. But the solubility was low in usual solvents ($CHCl_3$ THF, toluene, $CH_2Cl_2$, *etc.*). The molecular weight of the THF soluble fraction ranged from 7000 to 10 000.

The solubility may be increased by replacing one of the methyl groups by a long aliphatic chain to obtain a polymer containing flexible segments after condensation. Moreover both the interactions between side-chains and the free volume created by the side-chains in the material influence the physical properties. Two alkyl and three alkoxy side-chains were chosen and the starting materials were synthesized from mesitylene by a Friedel–Crafts reaction (**2** and **2′**) or from sodium 2,4,6,trimethylphenolate and the appropriate alkyl bromide by a Williamson (**3**,**3′** and **3″**) reaction. These substrates were characterized by elemental analysis, mass, IR, $^1$H and $^{13}$C NMR spectroscopy.

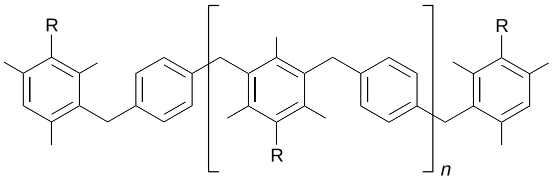


**2** R = $C_{16}H_{31}$
**2′** R = $C_8H_{17}$



**3** R = $C_{16}H_{31}$
**3′** R = $C_8H_{17}$
**3″** R = Bu

The stoichiometric (1 : 1) reaction between the substrate (**2**, **2′**, **3**, **3′** or **3″**) and *α*,*α*′-dichloro-*p*-xylene was performed in refluxing decane (174 °C) during 24 h in the presence of K10 Montmorillonite. After usual work up, removal of the catalyst and of the solvent, dissolution in the appropriate solvent and precipitation by MeOH, the polymers **P2**, **P2′**, **P3**, **P3′** and **P3″** were obtained respectively as white powders in *ca*. 60% yield. The solubility of these compounds increases with the length of the chain:



**P2** R = $C_{16}H_{31}$
**P2′** R = $C_8H_{17}$
**P3** R = $OC_{16}H_{31}$
**P3′** R = $OC_8H_{17}$
**P3″** R = OBu

**P3″** (THF, moderately) < **P2′** ($Et_2O$, moderately) < **P3′**, **P2** ($Et_2O$) < **P3** (heptane)

Elemental analyses and the IR, $^1$H and $^{13}$C NMR spectra of the crude materials are in agreement with the proposed formulae.‡ Note that these compounds contain a small amount of chlorine (*ca*. 0.1%), which could be due to terminal $-CH_2Cl$ groups of the macromolecular chains which were not quenched. The signal at 4.5 ppm due to a terminal $-CH_2Cl$ group is either extremely weak or not depicted. Consequently, the small amount of chlorine implies that most of the terminal groups are substituted phenyl groups.

The apparent volume of these polymers is strongly dependent on the length and the spatial position of the side-chains. It was thus very difficult to establish their molecular weight ($M_w$) by steric exclusion chromatography (SEC) using polystyrene samples as calibration standards. The polydispersity index ($I_p$) of the soluble fraction ranged from 1.3 to 2. Therefore, $M_w$ values were estimated from the NMR data: to each signal of the substituted phenyl group are joined signals of *ca*. 10 times lower intensity whereas the signal of the $C_6H_4$ protons is virtually unique: only a shoulder and two extremely weak signals (nearly 1% of the total integral value) were observed. The molecule is therefore linear, with a level of branching which does not exceed a few percent. The weak signals of the substituted phenyl group are due to the terminal groups (traces of residual polyalkylbenzene might also give such signals) and the minimal chain length and indeed the minimal averaged molecular weight can be deduced from the signals rate: *ca*. 20 units and 7000, respectively, for **P3′**. These results are also in good accordance with the molecular weight of **P1** (7000–10 000) determinated by SEC.

In conclusion, soluble polybenzyls can be synthesized by Friedel–Crafts polycondensation, using a non-toxic, mineral and removable catalyst. Their solubility should permit easy casting of thin films or coatings. Further experiments are in progress to enhance the macromolecular chain length of these polymers.

## Notes and References

† E-mail: baudryd@satie.u-bourgogne.fr

‡ Melting points were determined on a Kofler hot-stage apparatus. The weight-average molecular weight ($M_w$) of **P1** was obtained on a gel permeation chromatograph (Spectra Physics P200) connected to a Spectra Series UV 100 detector ($\lambda = 254$ nm) after calibration of the column using polystyrene standards (Polymer Laboratories). The column was a mixed PL-Gel column (particle size: 5 μm, pore type: 10 000 Å, length: 300 mm, internal diameter: 7.5 mm) with THF as solvent. The GPC Plus program was used to calculate the polydispersity index ($I_p$). $^1$H and $^{13}$C NMR spectra were recorded in $CDCl_3$ as internal reference ($\delta$ 7.25) on Bruker AC 200 (200 MHz) or DRX 500 (500 MHz) spectrometers. Mass spectra of the substrates were obtained on a GC–MS coupled spectrometer (Hewlett Packard G1800A) and elemental analyses on a EA 1108 CHNS-O (Fisons Instruments). The FTIR absorbance spectra were performed on a IFS 66v apparatus. The reactions were performed in a two necked-flask connected to a condenser. This flask was heated by a sand-bath and the mixture stirred by a magnetic stirrer. The condenser was connected to a drying tube for the substrates synthesis and to a HCl-trap for the polycondensations.

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