

Naphthalene Chemistry: II: A Novel Route for the Synthesis of Well Defined Star Block Copolymers Displaying an A(B)₂ Architecture from Hydrocarbon Monomers (A) and Ethylene Oxide (B).

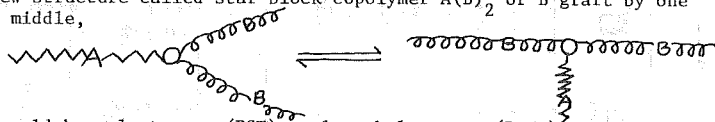
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Introduction:

It has been well demonstrated during the last decade that copolymer structure has a great influence on properties (1). In the case of colloidal and interfacial phenomena, NERVO (2) has pointed out the dependence of stability of emulsions and the size of dispersed particles on the molecular parameters such as molecular weight, composition and observed structure.

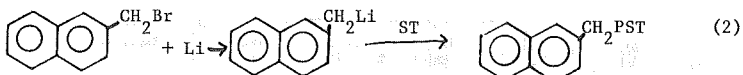
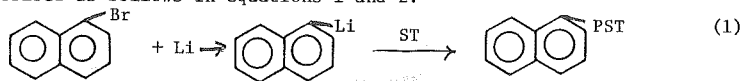
In the case of copolymers of styrene (A), and ethylene oxide (B), only well defined structures such as AB, BAB (1,2) or less defined B graft A (3) and A graft B (4,5) systems have been investigated. This paper is to report a new structure called star block copolymer A(B)₂ or B graft by one A in the middle,



where A could be polystyrene (PST), polymethylstyrene (P_MMS), poly-*p*-tert-butyl-styrene (PTBS) or polyisoprene (PIP), and B is polyethyleneoxide (PEO).

Results and Discussion:

In a previous paper, we have demonstrated that the dianion potassium of β -ethylnaphthalene can produce two PEO on the same naphthalene unit (6). The problem is to link quantitatively the naphthalene unit to the end of an A polymer. Two different methods have been proposed. The best results are generally obtained by using functionally substituted initiation (7) described as follows in equations 1 and 2.



Unsatisfactory results are obtained, however, due to the presence of secondary reactions such as wittig condensation (7), and attack of the living polymer end on the naphthalene nucleus (10). An added problem is the insolubility in non-polar media and instability in polar media (8,9).

The usual way is to deactivate a living polymer to a naphthalene bromo derivative such as Bromonaphthalene (1), β -Bromomethylnaphthalene (BMN), but the results are still insufficient due to the metal-halogen interconversion (12) (GPC 1 Fig. 1).

Richards has proposed to transform the living polymer to its Grignard analogue which is much less reactive, but still able to interact with the usual Bromoreagents (13,14) (eqs. 3,4).

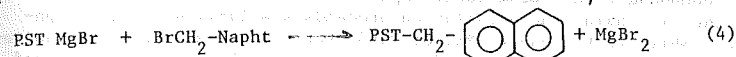
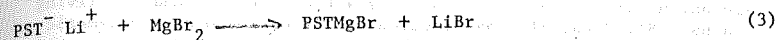
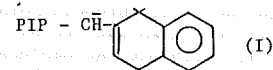
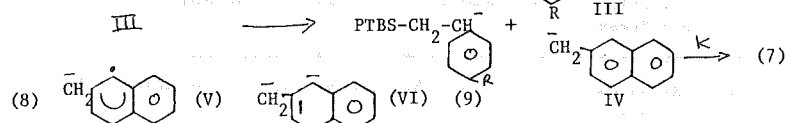
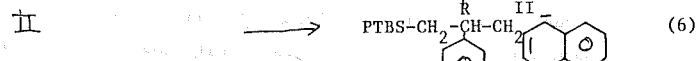
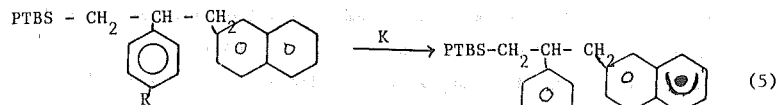


Fig. 1 and Table I shows that the polydispersity is low ($M_w/M_n < 1.1$) and the titration of end groups is quantitative (90%) (GPC 2). The metallation of the PIP-CH₂-Napht by sodium is limited to the anion radical state and the UV spectrum is identical to that of β -Ethyl-naph sodium (6). With potassium, it proceeds similarly as β -ethylnaphthalene:

Anion Radical (AR) dianion (DA) and finally isomerized dianion (6). The titration confirms the presence of two carbanions for naphthalene (Table II). One can state that changing the ethyl group to the PIP group does not change the course of the metallation. That is we represent the final stage by the following structure (I) (6,15).



The metallation of the PTBS-CH₂-Napht (or PST) by the potassium gives rise to four carbanions per naphthalene (Fig. 2). The UV spectra shown in Fig. 3 shows the formation of AR (UV9), PTBS K⁻ (1=365mm) and DA (1=440 mm) (UV10). The PTBS K⁻ undergoes living end isomerization (1=535 mm - UV = 11, 12, 13) (16, 17) which can be remetalated by K after hydrolysis (UV = 14). The mechanism of metallation can be summarized by equations: (5-9) which are well discussed elsewhere (15).



So, to obtain a stable dianion (or isomerized dianion), one can cap the living PTS or PTBS end by a few isoprene units before adding the naphthalene group.

The addition of EO to an isomerized dianion results in an A(B)₂ star block copolymer (Table III) in high yield (90%) (PP fraction). The homopolymer PA is only seven less than 10% (PF fraction) homopolymer of PEO can be avoided (PF fraction).

The PP fraction present a good correlation between predicted (NMR) and experimental (osmometric) mass molecular weight. The functionality is found to be 1.9. The GPC are shown in Fig. 4 where M_w/M_n is estimated lower than 1.25. The star block copolymers exhibit interesting surface active properties compared to the corresponding di and triblock copolymers (15).

Conclusion:

A naphthalene group can be successfully attached to the end of "living" polymer chains (PST, PTBS, PIP) by reaction of the corresponding polymeric Grigant compound with β -Bromomethylnaphthalene. When it is attached to the end of the PIP chain, the metallation proceeds similarly as β -ethylnaphthalene. While to the end of PST or PTBS, the naphthalene end group is released. The results are confirmed by UV spectra carbanions titration and hydrolysed products. In the case of dianion of naphthalene ended a PIP or PST-PIP or PTBS-PIP, an A(B)₂ well defined star block copolymer can be obtained in high yield.

Experimental Part:

See Ref. (6).

Acknowledgements:

The authors are very much indebted to Imperial Chemical Industries for efficient support through the first European Joint Project (including a fellowship to H. B. Gia). They also want to express their gratitude to Dr. S. Boileau (Laboratoire de Chimie Macromoleculaire, University de Paris VI) and Prof. J. E. McGrath (Virginia Polytechnic Institute and State University) Blacksburg, Virginia - USA for very fruitful discussions and review.

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Table II

POLYMER	N _n	[η] / [η] _{naph}
PIP	2100	2
PST-PIP	4800	2
PTBS-PIP	2900	2
PTBS-PIP	14800	1.95

Table I

POLYMER	N _n	FUNCTIONALITY (Z)
PIP	2100	90
PST	4800	89
	3400	92
PTBS	1900	92
	2800	90
	3400	95
	3700	95
	9600	90
	14800	88
	14800	38

Table III

Experiment No.	Fraction	% By Weight	% By Weight	% DE A* recuperated	N _n Theor.	N _n Practi
1	F	7	0	20	14,300**	
	15.5 gr A			trace of dihydro en UV		
	29.9 gr B (65% EO)		72		52,800 (14800*3800)	51,500
2	F	10	trace	25	1900**	
	8.9 gr A			15 which are dihydro (UV)		
	13.2 gr B (60% EO)		67		5700 (1900*3800)	5,500
	PF	trace				

* Percentage of recuperated PTBS based on the started weight of PTBS.

** Based on NMR measurement.

POLYCARBONATES FROM 1,1-DICHLORO-2,2-BIS(4-HYDROXYPHENYL)ETHYLENE
AND BISPHENOL-A, A HIGHLY FLAME RESISTANT FAMILY OF
ENGINEERING THERMOPLASTICS

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INTRODUCTION

The preparation of polycarbonates based on 1,1-dichloro-2,2-bis(4-hydroxyphenyl)ethylene (BPC) was first reported in 1964 as a copolymer with bisphenol-A (BPA) by Porejko et al (1), and later in 1968 as the homopolymer (2). In these and subsequent reports by these same workers (3-5), only a brief description was given of the physical and flammability properties of these polymers. In order to better define the properties of this system, these materials were prepared and evaluated. The results of this work are the subject of this paper.

SYNTHESIS

BPC is best synthesized by an acid catalyzed condensation of phenol with chloral to form 2,2-bis(4-hydroxyphenyl)-1,1,1-trichloro ethane, followed by HCl elimination. The condensation step is most conveniently carried out in a sulfuric acid/acetic acid mixture giving purified yields of up to 70% (2). Other acid systems such as anhydrous HCl (2,6), sulfuric acid/water (7a), sulfuric acid/methylene chloride (7b), acid ion exchange resin (8) and anhydrous HF (9) also are effective. The dehydrohalogenation step was most conveniently effected using methanolic KOH (2,10); however, other efficient base systems are liquid ammonia (11), LiCl in dimethylformamide (DMF) (12), and MOH (13) or M_2CO_3 (13) [M = Na or K] in DMF.

Early in this work it was discovered that the properties, especially color and impact, of the polymers made from BPC depended on the purity of this monomer (12). Thus, special care was taken to purify BPC by multiple recrystallizations, e.g., from MeOH/H₂O, until the required purity (12) was attained in ~70% yield.

Polymerization was performed using the standard interfacial technique (14) in methylene chloride. Copolymer systems containing various combinations of BPC and BPA were run without any change in procedure. Generally, 2.5 mole % of phenol was employed as a chain stopper yielding material whose intrinsic viscosity $[\eta]_{CHCl_3}^{25^\circ}$, ranged from 0.50 to 0.55 dl/g. Polymers made in this way were isolated by steam precipitation (15).

In order to make test parts, the above material was dried at 250°F for at least 3 hours in an air circulating oven, extruded into pellets at 510-550°F and injection molded using a melt temperature of 570°F and mold temperature of 200-205°F. Compression moldings, when required, were performed at 500°F.

PROPERTIES OF THE HOMOPOLYMER, COPOLYMER AND BPC-PC/BPA-PC BLENDS

The physical and the thermal and mechanical properties of the homopolycarbonate of BPC (BPC-PC) and the copolycarbonates of BPC and BPA, are tabulated in Table I. These data indicate that these polymers possess nearly the same attractive property profile as BPA polycarbonate (BPA-PC) and that the physical properties are virtually constant across the whole compositional range.

In the course of this work, it was found that BPC-PC was optically compatible in blends with a number of polyesters and polysulfones over a wide concentration range. Of particular interest, it was found that blends of BPC-PC and BPA-PC were optically compatible at all compositions and, as shown in Table II, show virtually constant mechanical properties over the total range.

