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Soluble, microporous ladder polymers formed by stepwise nucleophilic substitution of octafluorocyclopentene

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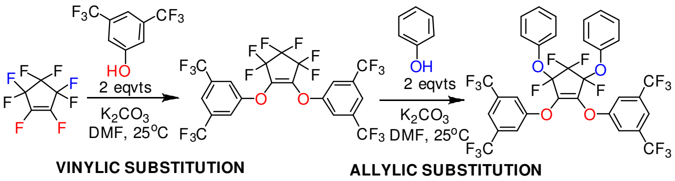
Octafluorocyclopentene (OFCP) has been demonstrated as a non-aromatic tetrafunctional monomer suitable for making soluble ladder polymers of intrinsic microporosity. Ladder polymers with varying surface area were prepared by reacting one mole of OFCP with 2 moles of bisphenols of same or different types. BET analysis of ladder polymers indicated that the surface area formed is comparable to that of microporous polymers derived from polyimides. MALDI-TOF MS indicated the presence of one OFCP and two bisphenols moieties in every repeating unit thereby confirming the presence of ladders in the polymer backbone.

Adsorption and separation of gases and liquids are important industrial processes where porous materials derived from activated carbon and zeolites play a significant role. Polymers of intrinsic microporosity (PIM) have been proposed as suitable substitutes for the abovementioned nanoporous materials.[1-2] Inherent characteristics of polymers such as ease of tuning of properties like surface area, pore volume, etc. along with ease of processing make them attractive alternatives. Other than gas separation applications, some of these PIM polymers bearing pendant $-SO_3H$ groups have also been explored as proton exchange membranes for fuel cell applications. [3] Although many classes of porous organic polymers have been reported, processing of these polymers to form membranes remains a challenge[4] because of the intractable nature of these polymers.

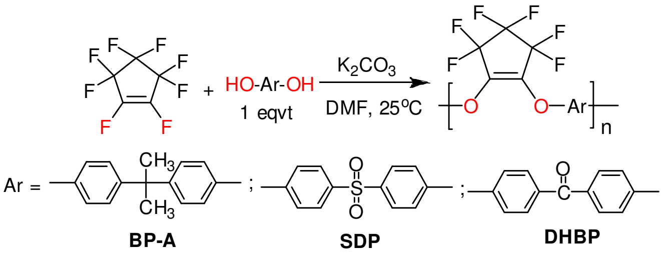
Organosoluble and thus solution processable ladder polymers of intrinsic microporosity is an important development in this area.[1,2] One of the methods of preparing solution processable PIMs is by reacting activated tetrafunctional phenols[5] and tetrafunctional fluoroaromatic compounds by nucleophilic aromatic substitution reaction. In order to fine tune the surface area and porosity characteristics of these solution processable porous polymers, substrates available for making such ladder polymers need to be broadened. In this regard, we hereby report the synthesis of soluble ladder polymers from a non-aromatic tetrafucntional monomer, octafluorocyclopentene (OFCP), with various bisphenols at room temperature or above room temperature (RT - 80 °C). These polymers are characterized using BET analyses to confirm their porous nature.

Octafluorocyclopentene (OFCP) contains eight fluorine atoms at 2:4:2 ratios in three different positions. OFCP has been reported to undergo nucleophilic substitution at vinyl position [1,5] previously by Smith Jr. et al.[6] In a subsequent publication, these authors have ruled out the allylic substitution of OFCP.[7] It has also been reported in literature that the ratio of vinylic to allylic substitution depends on factors like ring size, nature of nucleophile and reaction conditions employed, etc. More importantly, it has been reported that the formation of vinyl substituted product as major product is always favoured unless the allyl position has better leaving group.[8]



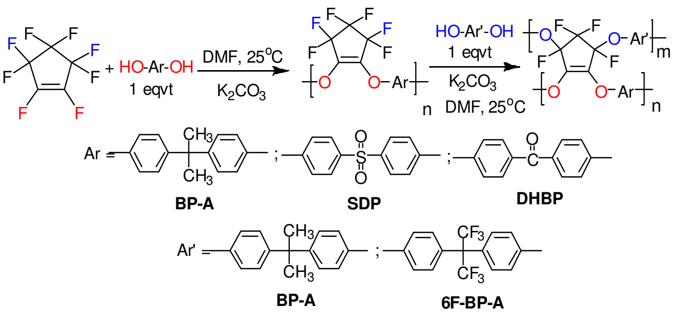
Scheme 1 Stepwise di- and tetrasubstitution of OFCP with (substituted) phenols at RT.

In contrast to the above observations, we have noticed that OFCP undergoes nucleophilic substitution of vinyl fluorine atoms in a facile manner under ambient conditions with two equivalents of (substituted) phenol. Allylic substitution occurs upon introducing two more equivalents of phenol of same or different type at room temperature or above (Scheme 1).



Scheme 2 Preparation of linear polymers by vinylic substitution.

This observation indicates that, the OFCP possesses not two replaceable F atoms as was reported earlier[6,7] but four replaceable F atoms. The ability to undergo such tetrasubstitution makes OFCP as a suitable, non-aromatic monomer for producing ladder polymers as well as hyperbranched or networked polymers.[9]



Scheme 3 Preparation of ladder polymers by two-step process.

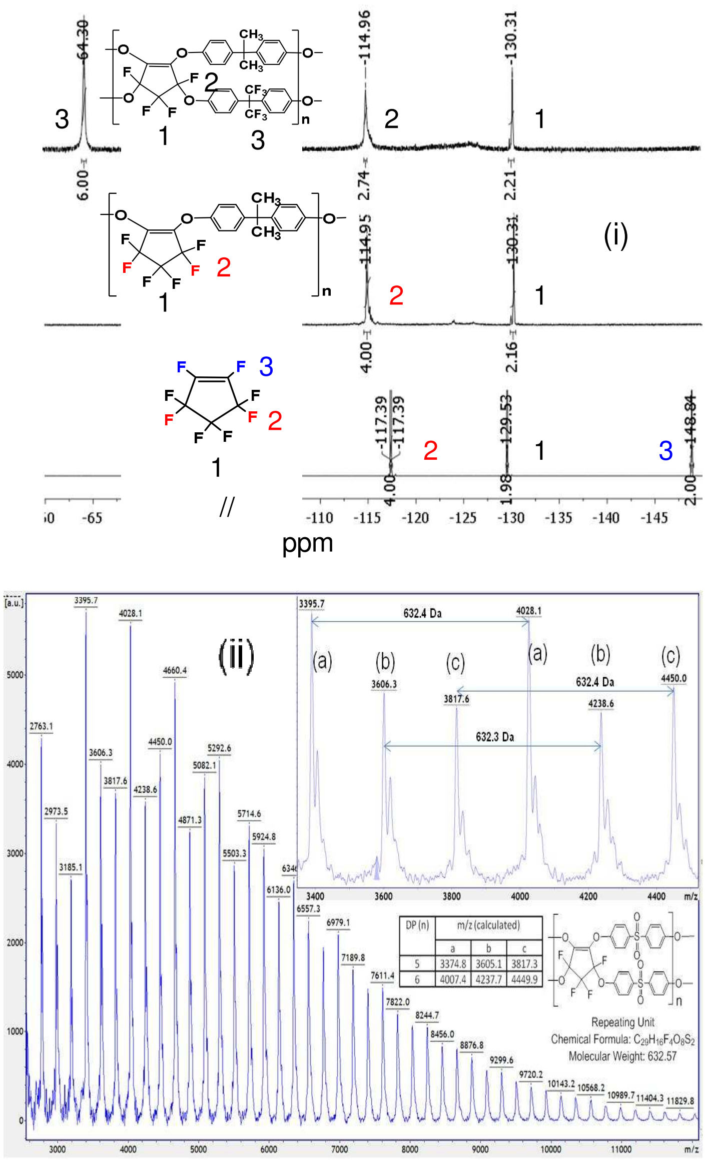


Fig. 1(i) ^{19}F-NMR spectra of OFCP (bottom), LIN P1 (middle) and LAD P1 (top). (ii). MALDI-TOF MS spectrum of ladder polymer sample (LAD P8).

Because of the absence of protons in OFCP, products formed by the substitution reaction with phenoxides generated *in situ* from phenols can be conveniently and conclusively analyzed by ^{19}F nuclear magnetic resonance (^{19}F-NMR) spectroscopy (Fig. S1). Fig. S1 unambiguously confirms the formation of di- and tetrasubstituted products.

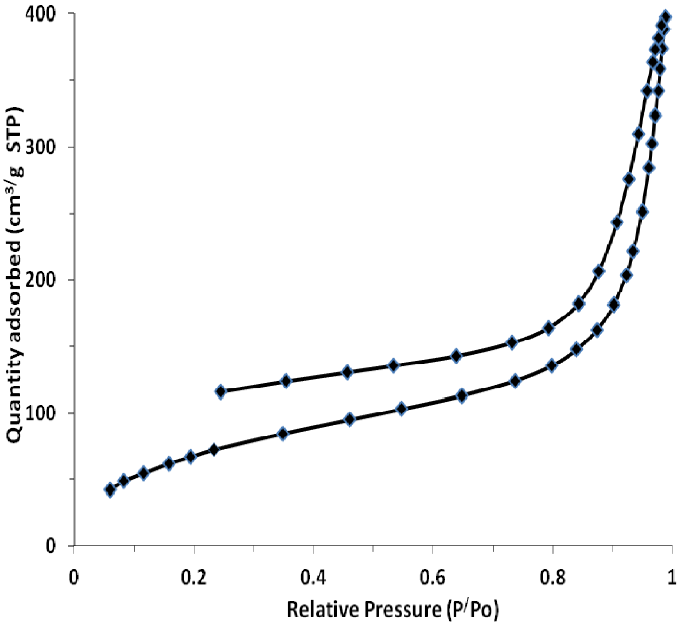


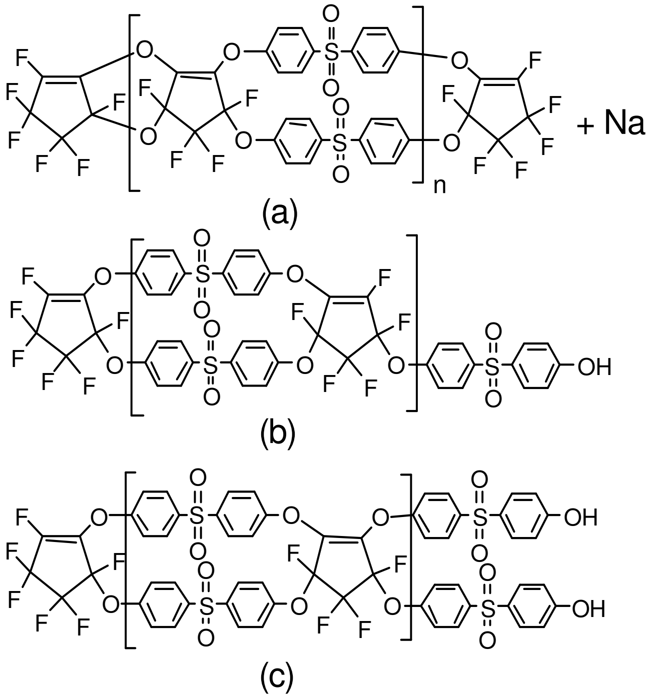
Fig. 2 The nitrogen adsorption/desorption isotherm of LAD P1.

Table 1 Characteristics of linear polymers formed by vinylic substitution of OFCP with different bisphenols at different conditions.

Polymer	Bisphenol	Temp (°C)	Yield (%)	^aM_n	^{a}PD
LIN P1	BP-A	25	70	5600	1.34
LIN P2		50	47	3500	2.00
LIN P3		80	64	7200	2.40
LIN P4	SDP	25	76	9000	2.08
LIN P5		55	60	3300	1.58
LIN P6		100	55	3300	1.58
LIN P7	DHBP	25	82	5600	1.53

(^{a}determined by GPC in THF eluent).

Reaction between OFCP and bisphenoxides formed *in situ* (1:1 mole ratio) resulted in the formation of low to moderately high molecular weight linear polymers as shown in Scheme 2. Highly acidic phenols like 4,4'-dihydroxydiphenylsulphone (SDP) yielded higher molecular weight polymers at room temperature (Table 1, LIN P4) compared to other bisphenols. The molecular weight decreased with increasing temperature (Table 1, LIN P4 Vs P5/P6) probably because of side reactions like allylic substitution as well as transetherification. However, stronger nucleophiles like *in situ* formed bisphenoxides derived from Bisphenol-A (BP-A) yielded comparatively higher molecular weight polymers at moderately high temperatures like 80 °C (Table 1, LIN P3). Further increase in temperature led to the formation of lower molecular weight polymers. The molecular weight of linear polymer LIN P3 is comparable to



Scheme 4 Ladder polymer chain end groups observed by MALDI-TOF MS analysis (LAD-P8).

Table 2 Molecular weight characteristic fragments observed in MALDI-TOF MS analysis (LAD-P8).

DP (n)	m/z (calculated)			m/z (observed)		
	series			series		
	a	b	c	a + Na$^+$	b	c
4	2742.3	2972.5	3184.8	2763.1	2973.5	3185.1
5	3374.8	3605.1	3817.3	3395.7	3606.3	3817.6
6	4007.4	4237.7	4449.9	4028.1	4238.6	4450.0
7	4640.0	4870.2	5082.4	4660.4	4871.3	5082.1
8	5272.6	5502.8	5715.0	5292.6	5503.3	5714.6
9	5905.2	6135.4	6347.6	5924.8	6136.0	6346.9
10	6537.7	6767.9	6979.6	6557.3	6768.7	6979.1
11	7170.3	7400.5	7612.1	7189.8	7401.2	7611.4
12	7802.9	8033.1	8244.7	7822.0	8034.2	8244.7
13	8435.5	8665.7	8877.2	8456.0	8666.4	8876.8

similar polymers reported previously[6,7] and obtained by using triethylamine as base. However the polymers obtained by using triethylamine exhibited narrow polydispersity similar to the polymers produced by anionic polymerization.

Linear cyclopentenyl aryl ethers (LIN P) were further reacted with one equivalent of bisphenoxides formed *in situ* to make ladder polymers as shown in Scheme 3. The incorporation of second bisphenoxide unit was confirmed by ^{19}F-NMR spectroscopy in the ladder polymer. The ^{19}F-NMR spectroscopy of linear and ladder polymers are given in Fig. 1(i). The ^{19}F-NMR spectrum of ladder polymers clearly indicated the incorporation of 6F-BP-A units in the polymer structure. Further we have analyzed these polymers using matrix assisted laser desorption and ionization time-of-flight mass spectrometry (MALDI-TOF MS) technique to establish the nature of chemical structure. In general, MALDI-TOF MS provides useful information on chain end-functionalities and also provides structural information such as linear, cyclic, ladder, etc., even for insoluble polymers.[10] MALDI-TOF MS of ladder polymer (LAD P8) is given in Fig. 1(ii). MALDI-TOF MS analysis of LAD P8 showed three types of structural arrangements as schematically represented in Scheme 4. Accordingly, three types of end groups existed. The ladder polymer was end capped with disubstituted OFCP at both ends (Scheme 4a), disubstituted OFCP and monosubstituted bisphenol at either end of the ladder polymer (Scheme 4b) and disubstituted OFCP and two monofunctional bisphenols (Scheme 4c) with the repeat unit showing molecular weight of 632.4 which corresponded to the ladder polymer containing tetrasubstituted OFCP with two bisphenols (Fig. 1(ii), inset). The ladder polymer molecular weights observed in MALDI-TOF MS and corresponding calculated molecular weights with three different polymer chain end-groups (Scheme 4) are shown in Table 2. A close correlation between observed and calculated molecular weights clearly indicates the presence of ladder structure in the polymer. As given in Table 3, molecular weight of the resulting ladder polymers increased with either moderate rise in polydispersity or without any appreciable change in polydispersity depending on the nature of bisphenoxide nucleophile employed in the second substitution reaction. The increase in molecular weight is due to the planarization of polymer backbone induced by the formation of ladder structures. Such planarization could lead to rigid backbones which in turn results in faster elution in chromatographic columns as compared to the more flexible linear polymer. The gel permeation chromatograms of linear and its corresponding ladder polymer obtained in a two-step process are given in Fig. S2 & S3. However, molecular weight reduction was noticed in LIN Ps derived from bisphenoxides bearing strongly electron withdrawing groups like sulphonyl due to the prevalence of transetherification reaction (Table 3, LAD P2).

Soluble ladder polymers have been reported to exhibit high surface area.[1a,1b] In general surface area of the polymers depends on structural features like rigidity and contorted shape. Polymers which are linear and also planar can pack efficiently leading to low surface area. The nitrogen adsorption/desorption isotherm of unsymmetrical ladder polymer, OFCP:BP-A 6F-BP-A (1:1:1 mole ratio) (LAD P1, Table 3) is shown in Fig. 2 (and also Fig. S4). The surface area of ladder polymers as determined by nitrogen adsorption at 77K by Brunauer-Emmett-Teller (BET) analysis is also given in Table 3. The surface area of ladder polymers varied between 36 and 269 m^2/g. The surface was predominantly determined by the nature of

Table 3 Characteristics of molecular weight, surface area and pore volume of ladder polymers.

Polymer	Step 1	T °C	M_n linear	PD linear	Step 2	M_n ladder	PD ladder	Yield (%)	Type	Surface area (m^2/g)	Pore volume (cm^3/g)
LAD P1	BP-A	25	7200	2.40	6F-BP-A	9800	2.50	52	unsymmetrical	199	0.54
LAD P2	SDP	25	9000	2.08	6F-BP-A	4000	1.50	88	unsymmetrical	36	0.09
LAD P3	DHBP	25	5400	1.50	6F-BP-A	9600	1.50	61	unsymmetrical	NA	
LAD P4	BP-A	25	7200	2.40	BP-A	8200	2.80	60	symmetrical	269	0.55
LAD P5*	BP-A	55	NA	NA	-	5900	1.50	33	symmetrical	57	0.23
LAD P6*	BP-A	100	NA	NA	-	5700	1.50	32	symmetrical	61	0.27
LAD P7*	SDP	25	NA	NA	-	3800	1.30	28	symmetrical	NA	
LAD P8*	SDP	55	NA	NA	-	4100	1.94	68	symmetrical	NA	

*one step procedure with 2 equivalents of bisphenols.

bisphenols employed. The surface areas are comparable in both unsymmetrical and symmetrical ladder polymers (Table 3, LAD P1 and LAD P4).

Polymers obtained by one step process as well those obtained from SDP as one of the nucleophiles showed low surface area. The low surface area is due to the prevalence of semi-ladder structures as indicated by the ^{19}F-NMR analysis and lower molecular weights. Polymers formed by a one step process, irrespective of reaction temperature exhibited similar surface area (Table 3, LAD P5 and LAD P6). The surface area of ladder polymers reported here are lower than that of soluble ladder polymers formed by nucleophilic aromatic substitution.[1,11] However, it is comparable to bisnaphthalene based soluble polyimides of intrinsic microporosity.[11] Recently, polyimides having structural features leading to poor chain packing and high chain rigidity have been reported to possess surface area of 270 m^2/g with total pore volume of 0.314 cm^3/g (at p/p^o=0.98, adsorption). Such polymers are proposed to be useful for high gas permeability with moderate selectivity.[13] The ladder polymers obtained by the nucleophilic substitution of OFCP are unique in that the surface area can be tuned substantially by the choice of bisphenol monomer as well as the mode of addition. BET analysis of these ladder polymers differed in two remarkable ways as compared to the soluble ladder polymers reported previously: (i). low hysteresis between adsorption and desorption curves. For example, low pressure hysteresis of 100 cm^2/g was noticed in the case of bisnaphthalene based soluble polyimides.[9] (ii). uniformly smooth desorption curve. Other reported PIM invariably showed two step desorption curves with the deviation occurring at midway through desorption of nitrogen gas. This was also noticed in a cross-linked polymer reported recently.[14] Hysteresis at low pressures has been attributed to pore network effects such as mesopores being accessible only through micropores.[1]

A steep rise in nitrogen adsorption was observed at high pressures. Such behaviour was also reported in polyimides and was explained as due to the condensation of nitrogen in the voids existing between precipitated particles of polymer.[11] The total pore volume estimated from the amount of gas adsorbed at p/p^o = 0.98 varied from 0.09 to 0.55 cm^3/g. The pore volume of LAD P6 was comparable to that of activated carbon (0.3 cm^3/g) and a polar zeolite, Zeolite 13X (0.31cm^3/g) though the surface area was far lower.[14] The pore volume of these ladder polymers were in general lower than that of other PIM.[1b,1c,11] Though the surface area of the ladder polymers reported here are lower than the PIM prepared by nucleophilic aromatic substitution the accessibility to pores is enhanced by the absence of pore network effects. It is useful to note here that porosity is also dependent on the method of processing the polymers with precipitated polymers showing better gas separation characteristics than the corresponding polymer films.

Conclusions

In summary, OFCP has been demonstrated to undergo tetrasubstitution with (substituted) phenols under mild conditions. The reaction between OFCP and *in situ* formed bisphenoxides yielded linear polymers through vinylic substitution at 1:1 mole ratio and resulted in soluble ladder polymers at 1:2 mole ratio along with allylic substitution as well in both single and two step processes. The surface area of polymers obtained can be tuned by the choice of bisphenol(s) and the reaction conditions. It may be possible to further fine tune surface area by modifications such as reduction of unsaturated bond. Currently efforts are underway in this direction as well as to prepare membranes for studying gas separation properties.

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Electronic Supplementary Information (ESI) available: This includes: experimental details of model reaction, linear and ladder polymer synthesis, characterization data of compounds, gel permeation chromatograms of linear and ladder polymers, and nitrogen adsorption/desorption isotherm of ladder polymers. See DOI: 10.1039/c000000x/

Notes and references

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