Synthesis and extremely high gas permeability of polyacetylenes containing polymethylated indan/tetrahydronaphthalene moieties†

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Received (in Cambridge, UK) 10th August 2007, Accepted 11th September 2007
First published as an Advance Article on the web 24th September 2007
DOI: 10.1039/b712327b

Polymethylated poly(diphenylacetylene) derivatives, a new category of substituted polyacetylenes, were successfully synthesized, and proved to show extremely high gas permeability.

Synthesis of substituted polyacetylenes has been the subject of intense interest because such polymers display unique physical and chemical characteristics and find potential applications as functional materials in optoelectronics, gas-separation membranes, stimuli-responsive materials, and other fields.[1] Recently, substantial research activity has been directed towards the precision synthesis of substituted polyacetylenes, namely, synthesis of acetylene-based living polymers and stereoregular and/or helical polymers.[2]

Membrane-based separation technology has attracted considerable attention in the past few decades[3] and substituted polyacetylenes constitute an important class of separation membrane materials.[4] These amorphous, highly stiff, glassy polymers are characterized by high gas permeability and high vapor/gas selectivity, which is strikingly different from conventional glassy polymers. One of them, poly(1-trimethylsilyl-1-propyne) (PTMSP), is the most gas-permeable polymeric material and many studies concerning the gas permeation properties of this polymer have been reported to date.[5] Poly(diphenylacetylenes) with bulky spherical substituents [*e.g.* poly[1-phenyl-2-(*p*-trimethylsilylphenyl)-acetylene] (PTMSDPA), its derivatives, and poly(1-β-naphthyl-2-phenylacetylene)] are another important category of substituted polyacetylenes, which exhibit excellent thermal stability and high gas permeability.[6] The unique permeation properties of these polymers are mainly attributed to their large excess free volume, which originates from their stiff main chain, bulky substituents, and low cohesive energy structure.[4,7] Since the discovery of PTMSP, various substituted polyacetylenes have been synthesized aiming at the development of even more permeable membrane-forming polymers. Although the incorporation of fairly bulky spherical groups such as trimethylsilyl and trifluoromethyl groups and the formation of sterically demanding structures have been recognized to favor high gas permeability, neither have the key factors driving the gas permeability been elucidated nor have polymers more permeable than PTMSP been found yet.

In this communication, we report the synthesis and extremely high gas permeability of polyacetylenes containing polymethylated indan [poly(1) and poly(2)] or tetrahydronaphthalene moieties [poly(3)] (Chart 1) and the most interesting feature is their extraordinarily high gas permeability despite the absence of spherical bulky moieties such as the trimethylsilyl group.

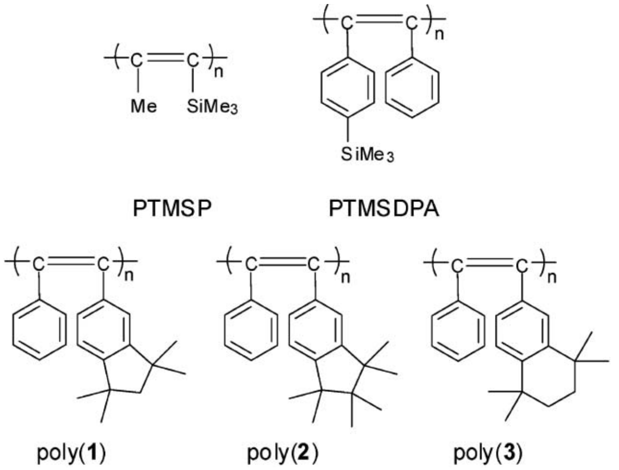

Chart 1

Polymerization of 1-(1,1,3,3-tetramethylindan-5-yl)-2-phenylacetylene (**1**), 1-(1,1,2,2,3,3-hexamethylindan-5-yl)-2-phenylacetylene (**2**), and 1-(1,1,4,4-tetramethyl-1,2,3,4-tetrahydronaphthalen-6-yl)-2-phenylacetylene (**3**) was carried out using $TaCl_5$–*n*-Bu_4Sn catalyst, which is effective for the polymerization of sterically crowded disubstituted acetylenes.[1a,1b] As shown in Table 1, all of the monomers **1–3** polymerized to afford polymers in moderate yields (43–67%) and the weight-average molecular weights (M_w) of the polymers were very high and ranged from 8.7×10^5 to 1.5×10^6. Poly(**1**) and poly(**2**) were soluble in common organic solvents including cyclohexane, toluene, and $CHCl_3$. On the other hand, poly(**3**) showed poor solubility and was soluble in $CHCl_3$ while being insoluble in cyclohexane and toluene.

Table 1 Polymerization of monomers **1**–**3** with $TaCl_5$–n-Bu_4Sn catalyst[a]

	Polymer[b]		
Monomer	Yield, %	$M_w \times 10^{-3\,c}$	M_w/M_n[c]
1	65	1000	3.9
2	67	1500	3.3
3	43	870	3.4

[a] Polymerization in cyclohexane at 80 °C for 24 h; $[M]_0$ = 0.20 M, $[TaCl_5]$ = 20 mM, $[n\text{-}Bu_4Sn]$ = 40 mM. [b] Methanol-insoluble product. [c] Determined by GPC, eluted with $CHCl_3$ (polystyrenes as standards).

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† Electronic supplementary information (ESI) available: Experimental details of the synthesis and characterization of the monomers and polymers. See DOI: 10.1039/b712327b

Table 2 Gas permeability coefficients (P) of the polymer membranes

	P (barrer[a])						
Sample	He	H_2	O_2	N_2	CO_2	CH_4	PO_2/PN_2
poly(**1**)	11 200	24 800	14 400	11 600	38 700	29 100	1.24
poly(**2**)	10 100	23 200	12 500	10 000	35 100	24 200	1.25
poly(**3**)	3500	7700	3900	2700	11 400	6600	1.44
PTMSP	9700	25 000	14 800	11 700	47 000	30 000	1.26

[a] Gas permeability coefficients at 25 °C in units of 1×10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) (= 1 barrer).

The IR spectra of the polymers did not exhibit the absorption at 2215 cm^{-1} ($\nu_{C\equiv C}$) which was observed in the monomers, indicating that the triple bond of the monomers was completely consumed during the polymerization and converted to alternating double bonds along the main chain in the polymers. The present polymers showed two characteristic UV–Vis absorption maxima ($\lambda_{max,abs}$) around 375 and 430 nm, which are due to the π–π^* transition of the conjugated system. The cut-off wavelength is approximately 500 nm, indicating that the conjugation of the polymer is relatively short.[6a] The onset temperatures of weight loss of poly(**1**), poly(**2**), and poly(**3**) were 410, 440, and 400 °C, respectively, which are obviously higher than that of PTMSP (300 °C),[5b] showing that these polymers have excellent thermal stability.

Free-standing membranes were fabricated by casting poly(**1**) and poly(**2**) from toluene solution, and poly(**3**) from $CHCl_3$ solution due to the difference in their solubility. The gas permeability coefficients of the membranes are listed in Table 2. The oxygen permeability coefficients (PO_2) of poly(**1**) and poly(**2**) were as high as 14 400 and 12 500 barrers, respectively, which are about the same as that of PTMSP measured under the same conditions. Typical PO_2 values of PTMSP and PTMSDPA have been reported to be around 10 000 and 1500 barrers, respectively.[4a,4b] When poly(**1**) was kept in a polyethylene sack in the dark at room temperature, the PO_2 value decreased to 10 800 barrers after 60 days. The PO_2 of PTMSP decreased to a similar extent (12 000 barrers) under the same conditions. The following points are worth mentioning: (i) these two polymers show extremely high gas permeability comparable to that of PTMSP, although the structures of the present polymers are quite different from that of PTMSP, (ii) poly(**1**) and poly(**2**) are the most gas-permeable among all the aromatic polyacetylenes, and the presence of the phenyl ring does not necessarily depress the gas permeability, while many aromatic polyacetylenes without ring-substituents are much less permeable (*e.g.* poly(phenylacetylene) $PO_2 = 6.0$ barrers[8]), and (iii) although it was thought before that the presence of relatively bulky spherical groups such as trimethylsilyl and *t*-butyl favors high gas permeability, the present findings reveal that the presence of many methyl groups has a similar effect. The PO_2/PN_2 ratios of poly(**1**), poly(**2**), and PTMSP remain around 1.25, and a trade-off relationship is observed between permeability and permselectivity.[9] The PO_2 value of poly(**3**) is about a quarter of those of the other polymers in the present series, and is also fairly large among those of various substituted polyacetylenes. The PO_2/PN_2 ratio of poly(**3**) is 1.44 which is slightly larger than those of poly(**1**) and poly(**2**), corresponding to the trade-off tendency. Keeping in view the experimental findings, it is inferred that a plural number of methyl groups in the present polymers generated sufficient excess free volume and exhibited a large local mobility as well through their rotation, thus facilitating the diffusion of gases.[10]

In summary, we have successfully synthesized a new category of substituted polyacetylenes, polymethylated poly(diphenylacetylene) derivatives. Among them, the indan-containing aromatic polyacetylenes exhibited extremely high gas permeability, comparable to that of the most permeable PTMSP, although they have no bulky substituents such as the trimethylsilyl group. The discovery of high gas permeability of these polymers will provide valuable information for the future development of highly gas-permeable polymeric materials. A detailed investigation of the synthetic aspects and properties of these polymers is currently underway.

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