Poly(vinylspirobifluorene): Synthesis and Properties of a Novel Styrenic Polymer

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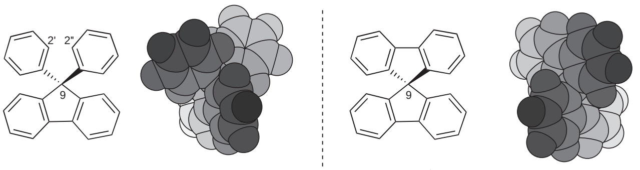
Synthesis and properties of a new class of styrenic polymer are reported. The radical polymerization of 2-vinyl-9,9′-spirobifluorene yielded high molecular weight poly(vinylspirobifluorene) with high thermal stability and high solubility, which gave a self-standing transparent film with high refractive index.

Polymers containing 9,9-diarylfluorene (DAF) moieties, so called "cardo" structure, in the main chains are an intriguing class of polymers owing to their attractive nature. The "cardo" polymers have recently generated particular interest due to their characteristic properties such as high refractive index,[1] low birefringence,[1] high solubility, high thermal stability, and fine dispersing ability toward fillers.[2] Meanwhile, 9,9′-spirobifluorene (**2**) (SBF) is a spirocyclic derivative of 9,9-diphenylfluorene (**1**), of which two phenyls are connected at their C2′ and C2″ positions through C–C bonds (Figure 1). The structure of **2** consisting of the vertically crossing fluorene moieties is expected to display both high refractive index and low birefringence by the high dense aromatics and cancellation of optical anisotropy like **1**. Several studies directed toward optical use have been reported,[3] in which the spirocyclic structure enabled suppression of π aggregation or excimer formation, leading to most promising blue-light emitting materials. We have also developed general entries to polycarbonate and polyesters possessing 9,9-spirobifluorene skeletons in the main chains.[4,5] It turns out that the resulting polymers contain the requisite moieties of defined hindrance to minimize interchromophore interaction. Among monomers having SBF skeletons in the side chains, vinyl monomer directly attached by the SBF moiety seems the most fundamental polymerizable derivative of **2**. Herein, we report the synthesis and polymerization of 2-vinyl-9,9′-spirobifluorene and properties of the resulting polymer. A few typical optical properties such as transparency and refractive index are also evaluated in addition to the thermal properties.

Synthesis of monomer 2-vinyl-9,9′-spirobifluorene (**4**) from 2-bromo-9,9′-spirobifluorene (**3**)[6] was achieved by Stille coupling exploiting tributylvinylstannane in the presence of $Pd(PPh_3)_4$ (5 mol %) as the catalyst (91% yield).[7]

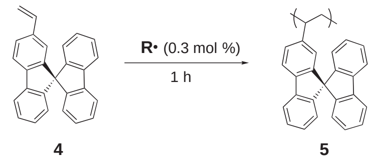
Radical polymerization of **4** in the presence of a radical initiator was conducted in toluene or DMF.[7] Polymer **5** was obtained as a white powder insoluble in methanol. The results are summarized in Table 1. The polymer **5** was readily soluble in common organic solvents such as toluene, $CHCl_3$, DMF, and THF similar to those having DAF or SBF moieties, while the polymer solution was highly viscous in any case. Polymerization with 2,2′-azobis(isobutyronitrile) (AIBN) afforded **5** with higher molecular weight (Entry 1, 82% yield, M_n 109000, M_w 561000, M_w/M_n 5.2) than those obtained with benzoyl peroxide (BPO) in each solvent. The high polymerizability of **4** in solution polymerization seems to come from the slow termination arising from the low degree of bimolecular coupling due to the bulky propagation end of **4**. The light-scattering measurement for **5** indicated the rather low Mark–Houwink's a value of 0.49, suggesting that polymer **5** does not take a rigid rod linear form, even though the polymer has a big pendant group.



9,9-Diphenylfluorene (**1**) 9,9′-Spirobifluorene (**2**)

Figure 1. 9,9-Diphenylfluorene (**1**) and 9,9′-spirobifluorene (**2**): chemical (left) and MM2-simulated (right) structures.

Table 1. Synthesis of poly(2-vinyl-9,9′-spirofluorene) (**5**)



Entry	Iniciator	Solvent	Temp/°C	Yield/%	M_n ($\times10^3$)[a]	M_w ($\times10^3$)[a]	M_w/M_n[a]
1	AIBN	Toluene	70	82	109	561	5.2
2	AIBN	DMF	70	78	103	328	3.2
3	BPO	Toluene	90	22	30	96	3.2
4	BPO	DMF	90	24	33	96	3.0

[a]Estimated by GPC based on PSt standards.

The structure determination of **5** was performed by ^{1}H NMR, ^{13}C NMR, CPMAS, and IR spectra.[8] Both aliphatic proton signals on the ^{1}H NMR spectrum of **5** disappeared most likely owing to effective coverage of the main chain by the pendant groups or the coalescence rotamers of the pendant groups. In addition, all aromatic proton signals became a broad and unassignable signal. On the other hand, relatively clear carbon signals were obtained in both the liquid-state ^{13}C NMR and the CPMAS spectrum (Figure 2).[7] The IR spectrum of **5** showed typical aromatic and aliphatic C–H absorptions at 3061 and 2921 cm^{-1}.

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed for the evaluation of thermal property of **5** (Entry 1). DSC showed a high glass-transition temperature (T_g 289 °C) without any melting point, while TGA showed a high 5% weight loss point (T_{d5} 419 °C). The high thermal stability of **5** seems to come from the presence of SBF moieties in accordance with the previously reported results.[1,2] It should be noted, however, that polymer **5** possesses the SBF groups in a side chain not in the main chain. This is the first example of the side chain type SBF polymer, and thereby we can conclude that the incorporation of the SBF group into polymer contributes to enhancement of its thermal stability

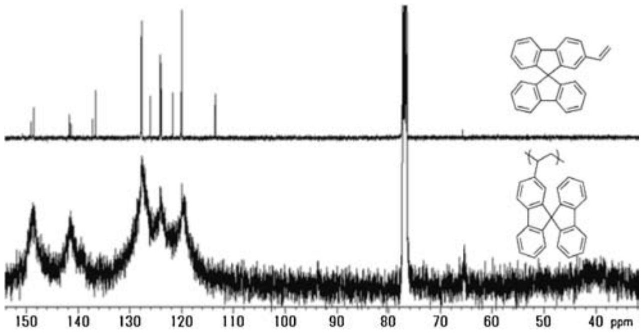
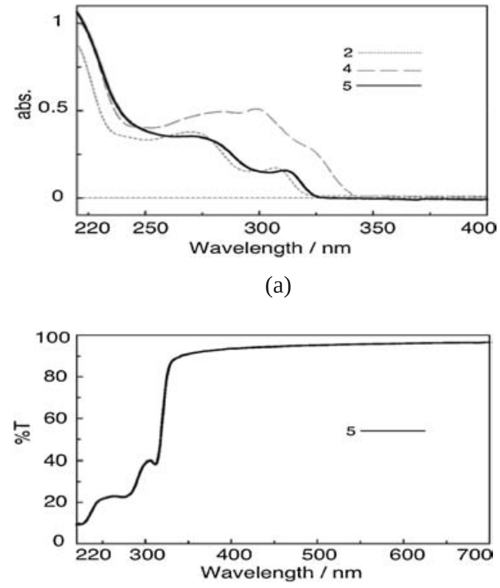


Figure 2. ^{13}C NMR spectra of **2** and **5** (100 MHz, $CDCl_3$, 298 K).



(a)

(b)

Figure 3. UV–vis spectra (a) of **2**, **4**, and **5** (20 μM, THF, 298 K) and transmittance of **5** (b) were obtained by the measurement in a scanning width ranging from 200 to 700 nm with UV–vis spectrophotometer.

independent of whether it is placed on the main chain or side chain, probably owing to the effective intramolecular packing to disturb a random walk.

A broad UV–vis absorption around 330 nm observed for **4**, not for **2** or **5**, corresponded to the extended π conjugation due to the vinyl moiety of **4** (Figure 3a). Similar UV–vis spectra of **2** and **5** probably suggests that the steric hindrance of SBF moiety tends to minimize the interchromophore interaction. Self-standing polymer film of **5** obtained by casting from chloroform solution was sufficiently transparent to reach over 90% transmittance in the range of 325–700 nm (Figure 3b). The fluorescence spectrum of **4** showed an emission around 350 nm much strongly than **2** and **5**,[8] presumably due to the extended conjugation by the vinyl moiety added to **2**. On the other hand, the fluorescence spectrum of **5** was approximately similar to **2**, which is also consistent with the largely decreased interchromophore interaction in the polymer chain.

Refractive index of **5** was sufficiently high: 1.61 at a typical wavelength of 589 nm, in comparison with those of representative vinyl polymers. The markedly high refractive index of **5** is probably attributable to the nature of the polynuclear aromatic group of the SBF skeleton.

In summary, this paper has disclosed the synthesis and radical polymerization of a novel styrenic monomer bearing a directly attached SBF group. Poly(vinylspirobifluorene) **5** with high molecular weight and high viscosity in solution was a flexible linear polymer as suggested by the low Mark–Houwink's *a* value. The characteristic properties of **5** feature high transparency and high refractive index in addition to high solubility and high thermal stability. Thus, the present study clearly demonstrated that the introduction of the SBF moiety into not only polymer main chains but also side chains induces useful properties into the polymer.[9] Synthesis of stereoregular polymers from **4** in relation to polymerization methods would be important future work from the viewpoints of control of polymer structure and property.

References and Notes

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