doi:10.1246/cl.2010.2

Highlight Review

9,9-Diarylfluorene Moiety Incorporated into Polymer Main Chains: An Essential Skeleton Exhibiting Prominent Physical, Chemical, and Optical Properties

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(Received September 18, 2009; CL-098010)

Abstract

The present review summarizes the prominent properties, in particular, the unique optical properties, generated by 9,9-diarylfluorene moiety introduced into polymer main chains in addition to the synthesis of polymers containing diarylfluorene moieties on the basis of results of the studies reported mainly in this decade. Polymers usually show both high refractive index and low birefringence besides many other physical and chemical properties. This review focuses not only on the polymers but also the composite materials, and discloses excellent polymer materials. In addition, synthesis and properties of novel related monomers and their corresponding polymers are also described.

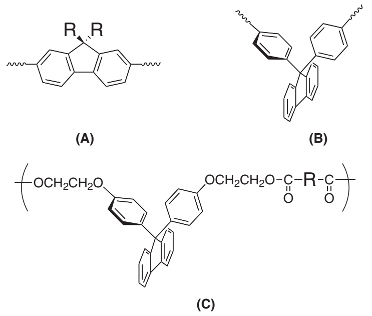

Figure 1. Fluorene skeletons incorporated in polymers **A** and **B** and corresponding polymer **C**.

◆ 1. Introduction

Currently, syntheses, properties, and applications of fluorene skeleton containing polymers have been under active investigation. While most of the polymers involve 2,7-connected fluorene skeletons in their main chains (**A**), polymers possessing the 9,9-connected fluorene structure (**B**) also have attracted much interest as promising useful polymers where the fluorene moiety is attached directly to the main chain at the 9-quaternary carbon as a pendant group (Figure 1).[1] Polyesters (**C**)[2] and epoxy resins[3] consisting of **B** play important roles in the fields of electronic and optical materials.

Polymers involving the **B** moiety consisting of the 9,9-diarylfluorene structure, called the *Cardo* structure,[4] usually show unique optical properties of both high refractive index and low birefringence, thus being different from those expected from many aromatic groups with high polarizability.

Besides these optical properties, the polymers can be characterized by superior thermal stability, solubility, and amorphous, transparent nature, in addition to the low degree of thermal expansion. Furthermore, polyurethane with the **B** moiety is not brittle even at very low temperatures.[5] On the other hand, the polymers of **B** have such excellent miscibility toward many other polymers that they can be used as compatibilizers. Another additional remarkable property is the achievement of high dispersion of organic and inorganic fillers due to extraordinarily high affinity toward the fillers, suggesting a wide range of applicability as composite matrix resin. The characteristic properties of the polymers containing the **B** structure are summarized as follows:

(1) Physical and chemical properties: amorphous nature and high solubility.

(2) Optical properties: high transparency, high refractive index, and low birefringence.

(3) Thermal properties: high thermal stability, low degree of thermal expansion, and flexibility at very low temperatures.

(4) Affinity toward other materials: high miscibility and high filler-dispersing power.

We focused on their prominent properties and have studied the synthesis and properties of a variety of polymers in addition to the development of novel monomers. This review article summarizes the syntheses of monomers and polymers containing 9,9-diarylfluorene (DAF) structures, and their unique properties with special emphasis on the optical properties, reported mainly in this decade.

◆ 2. Construction of DAF Skeleton

The synthetic methods of **3** (Scheme 1) are mainly divided into two approaches. The first approach is through Lewis acid-catalyzed nucleophilic substitution of aromatics such as phenol or aniline derivatives **2** to 9-fluorenone **1**, which enables an efficient conversion in the presence of a catalytic amount of 3-sulfanylpropionic acid to the corresponding homoditopic **3**.[6] The second approach utilizes Pd-catalyzed coupling reaction of fluorene **4** with aryl halides **5**,[7] in which the use of Pd(OAc)$_2$ as

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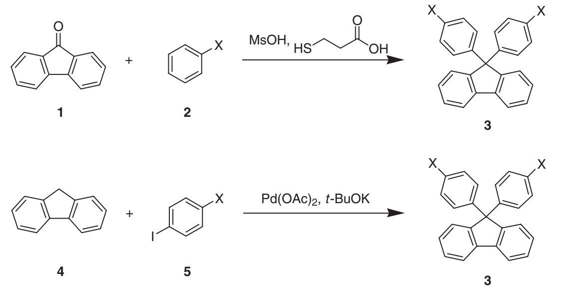


Scheme 1. Synthesis of DAF monomer **3**.

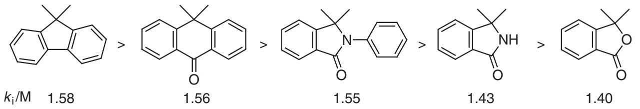


Figure 2. Thermal stability of *Cardo* moiety.

a catalyst in the presence of t-BuOK efficiently renders sequential coupling at the 9 position of fluorene to afford the corresponding **3**. Today, several DAF containing monomer **3** are commercially available.

◆ 3. Properties of DAF Containing Polymers

There are many reports concerning the synthesis and the characteristic properties of the main chain-type polymers by exploiting polycondensation of the homoditopic **3** as mentioned above.

3.1 Thermal Stability

The thermal properties of *Cardo* structure containing polymers have been extensively investigated theoretically and experimentally, indicating high thermal stability. In particular, it is found that DAF containing polymers are the most thermostable of the related polymers. The glass transition temperature (T_g) of polymers follows well the empirical rule: $\log T_g = d\Sigma k_i/M - A$, where d denotes the density; Σk_i, constant for each element in the composition of the polymer molecule; M, molecular weight of the repeating unit; and A, constant depending on the series of polymers. On the basis of this equation, Korshak et al. mentioned that the decreased volumes of aromatics per molecular weight ($\Sigma k_i/M$) were clearly dependent on T_g.[8] Figure 2 shows the calculated values of $\Sigma k_i/M$, which suggests that the fluorene skeleton is the most heat resistant in a series of *Cardo* structures.

In fact, DAF containing polymers show high thermal stability resulting from the rigid structure of the monomer.[9] Morgan et al. confirmed the relative thermal stability to the *Cardo* structure, including the softening temperature and decomposition temperature (Figure 3).

The softening temperatures of polyesters with *Cardo* structures are higher than those of polymers without the structure, due to the rigid skeleton disturbing free movement of the polymer chain. In particular, DAF containing polyester **9** shows a higher softening point compared to polymers with other *Cardo* moieties.

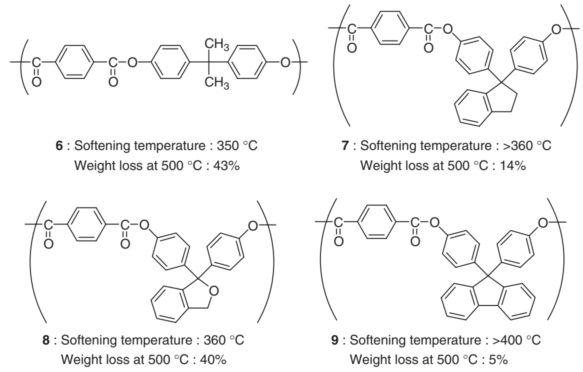


Figure 3. Thermal properties depending on *Cardo* moiety.

On the other hand, the 5% weight-loss temperature of **9** appears at 500 °C, which is in remarkably high contrast to those of other polyesters, strongly suggesting that the introduction of DAF moieties into the polymer efficiently leads to a heat-resistant polymer.

3.2 Solubility

The solubility of DAF containing polymers toward organic solvents is high. This comes from the amorphous inherence of the polymers attributed to the bulky DAF structure because of the *Cardo* structure in the main chain, to prevent intra/intermolecular interactions and enhance solvation.[10]

3.3 Optical Properties (Transparency, Refractive Index, and Birefringence)

DAF containing polymers display high transparency resulting from their amorphous nature, because the bulky *Cardo* structure suppresses intra/interchromophore interaction between polymer chains. Moreover, the polymers show both high refractive index and low birefringence.[11] Since the studies of low birefringence originating from the DAF structure were reported by Sakurai et al., related investigations of optical properties have accelerated.

Sakurai et al. studied the effects of copolymer composition on the optical properties such as the refractive index and birefringence of the copolymers[2a,12] prepared from 9,9-bis-[4-(2-hydroxyethoxy)phenyl]fluorene (BPE) and dimethylterephthalate with ethylene glycol (Table 1).

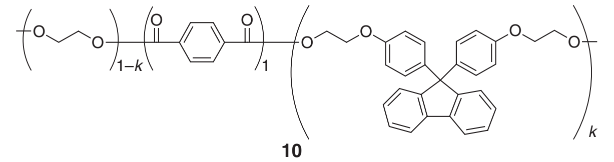
As the composition ratio of DAF structure increases, the refractive indices of the copolymers **10** increase, while the intrinsic birefringence values decrease; clearly indicating promising properties of the DAF structure toward the suppression of birefringence.

Han et al. investigated the optical properties of polyimides using the spin-coating films (Figure 4).[11c]

While the X-ray diffraction (XRD) profiles of polyimides **12** and **13** have several peaks originating from the partial crystal structure that of DAF containing polyimide **11** shows a broad signal as the amorphous inherence. The birefringence of **11** is 0.012, whereas the refractive index is low (1.57).

Kim et al. synthesized fluorine containing poly(arylene ether)s from bis(pentafluorophenyl) sulfide and various bisphenols (Figure 5).[11f] Although fluorine containing polymers generally show low refractive indices, DAF containing polymer **14**

Table 1. Effects of copolymer composition on intrinsic birefringence



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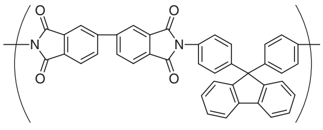
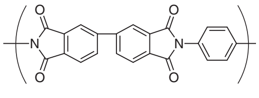
Entry	Copolymer composition (k)[a]	Refractive index[b]	Intrinsic birefringence
1	0.11	—	0.161
2	0.21	—	0.115
3	0.40	1.620	0.077
4	0.61	—	0.072
5	0.70	1.630	0.068
6	0.81	—	0.064
7	0.93	—	0.058

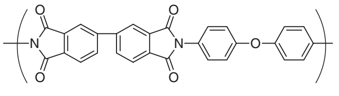
[a] From ^{1}H NMR. [b] Evaluated at 589 nm.



11 (n 1.57, Δn 0.012)

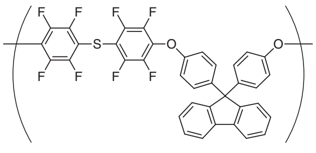


12 (n 1.77, Δn 0.236)

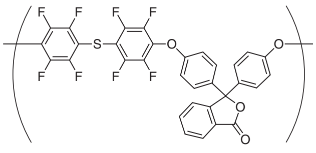


13 (n 1.73, Δn 0.067)

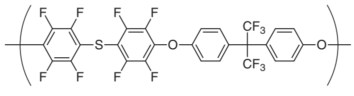
Figure 4. Optical properties of polyimides.



14 (n 1.617, Δn 0.0009, δ0.132)



15 (n 1.598, Δn 0.0012, δ0.197)

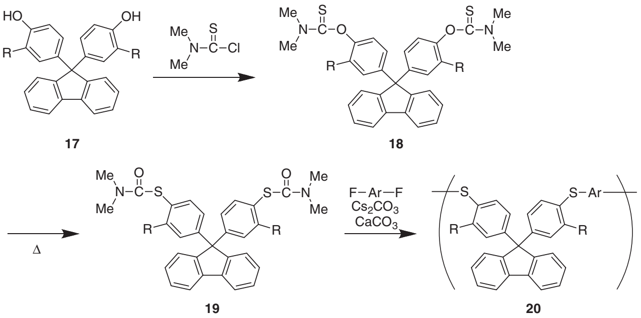


16 (n 1.541, Δn 0.0025, δ0.334)

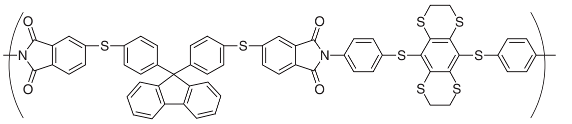
Figure 5. Optical properties of poly(arylene ether)s.

shows a fairly high value over 1.60. Interestingly, the birefringence value of **14** is much lower than those of other polymers with the *Cardo* structure. To estimate the origin of these results, PM5 calculations were conducted to evaluate the polarized ratio (δ) proportional to the birefringence value. The results indicate that the value of **14** is smaller than that of **15**. That is, the introduction of DAF structure is useful to decrease the optical anisotropy and birefringence.

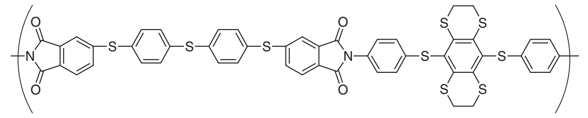
Takata et al. prepared DAF containing poly(arylene sulfide)s **20** from masked DAF dithiol **19** that yielded DAF dithiol in situ to react with difluroroarenes, and to finally yield polythioethers with high molecular weights. These poly(arylene sulfide)s **20** show high refractive indices in a range from 1.66 to 1.72 along with zero birefringence values (Scheme 2).[11h]



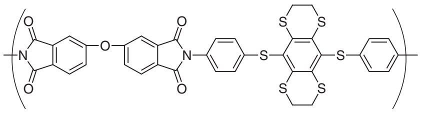
Scheme 2. Synthesis of sulfur containing polymers using masked dithiols.



21 (n 1.742, Δn 0.0070)



22 (n 1.769, Δn 0.0093)



23 (n 1.741, Δn 0.0108)

Figure 6. Optical properties of sulfur containing polymers.

On the other hand, Ueda et al. synthesized sulfur containing polyimides from monomers possessing many sulfur atoms (Figure 6). The spin-coated polyimide films were obtained using high temperature imide formation.[11i,11j] These polyimides show high refractive indices in the range of 1.74 to 1.77, originating from the introduction of many aromatics and sulfur atoms and the increased density of the polymer caused by the planer thiaanthrathene-like moiety containing many sulfur atoms. The birefringence values of DAF containing polymer **21** are low (7.0×10^{-3}), indicating the fruitful effects of the introduction of the DAF structure on the optical properties.

Because the structures other than DAF structures generate birefringence in DAF containing polymers as reported by Sakurai,[2a,12] zero birefringence of the polymer should be achieved by introducing spacers without any optical anisotropy. For this purpose, Takata et al. investigated the effects of the structure of alkylene chains in DAF containing polyether on the refractive index and birefringence in detail (Figure 7).[13]

These polymers **24** show higher refractive indices as the spacer length is shortened. On the basis of the Lorentz–Lorenz equation, the results are explained by the reduced density of the polymer by the introduction of long alkylene chains. These polymers show birefringence less than 1.3×10^{-5} at 590 nm.

Moreover, Takata et al. reported the introduction of a comonomer unit with high refractive index and low birefringence to the DAF containing polymers (Figure 8).[14] The

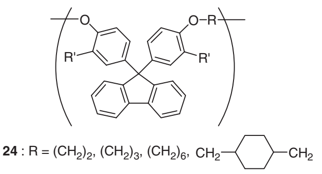


Figure 7. DAF containing polyethers **24**.

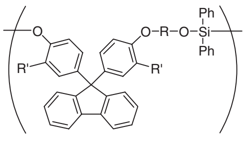


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Figure 8. DAF containing polysiloxanes **25**.

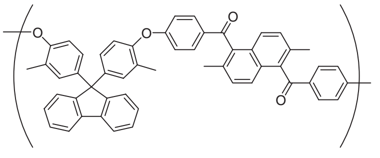

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Figure 9. DBDMN and DAF containing poly(ether ketone) **26**.

introduction of diphenylsilylether moieties to a DAF polymer affords the corresponding polysiloxane **25** with high refractive index and zero birefringence at both drawn and undrawn states.

It turned out that the slightly bulky 1,5-dibenzoyl-2,6-dimethylnaphthalene (DBDMN) unit, which disturbs the intra/interchromophore packing, is also a promising candidate as a comonomer moiety. In fact, poly(ether ketone) with DAF skeleton **26** shows high refractive index (1.646) and zero birefringence (Figure 9).[15] The refractive index is fairly high despite the polymer structure consisting only of C, H, and O atoms.

The alloys of DAF containing polyester **27** with bisphenol A polycarbonate (PC) causes a remarkable decrease in birefringence (Figure 10).[16] These blended samples show one T_g, indicating the formation of single phase. The orientational birefringence values decreases as the added ratio of **27** to PC increases. Finally, the alloy formed by the addition of 40 wt % of **27** shows almost zero birefringence, strongly suggesting the significance of not only copolymerization but also alloyment of the DAF polymer for enhancing the optical properties.

Thus, while DAF containing polymers show high refractive indices originating from many aromatics, these polymers display low birefringence resulting from the *Cardo* structure of the DAF moiety, providing promising optical material candidates with excellent chemical and physical properties.

◆ 4. Polymer Composite and Alloy Utilizing DAF Containing Polymers

Polymer composites and alloys with carbon material, dye, pigment, metal, ceramics, and glass fiber have recently received increasing importance. Such techniques can create high performance polymeric materials by improving the properties of the matrix polymer such as the mechanical strength, conductivity, and optical properties.

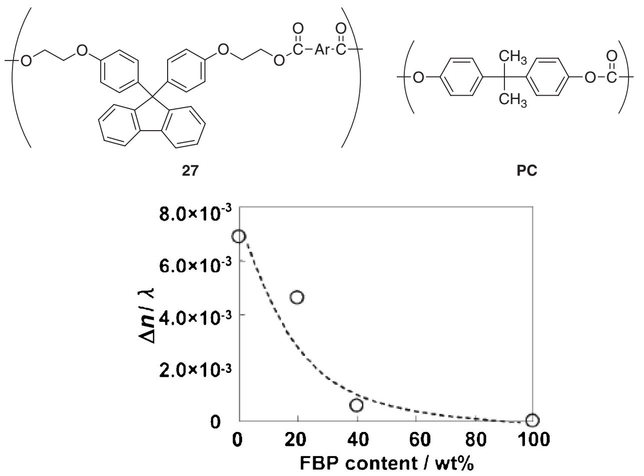

Figure 10. Relationship between the orientational birefringence ($\Delta n/\lambda$) and the content of **27** in alloy sheets.

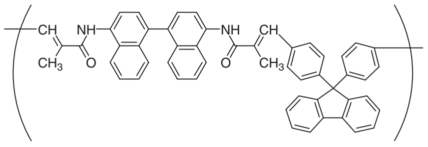

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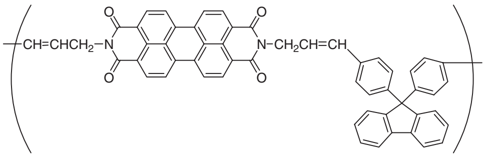
Figure 11. Structure of **28**.



29

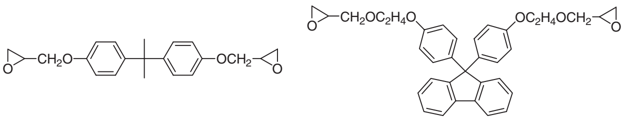
Figure 12. Structure of **29**.

4.1 Filler-dispersing Ability of DAF Containing Polymer

DAF containing polymers can be characterized by good affinity to fillers due to large π-space consisting of many aromatics. In fact, the good filler dispersion of DAF containing epoxy resin has been reported.[3c,17]

Chen et al. measured fluorescent spectra of carbon filler composites of **28** (Figure 11), which consists of good luminous DAF units and thermally stable methacryloylamidobinaphthyl units.[18] With increasing concentration of C_{60}, the fluorescence of **28** was efficiently quenched, suggesting strong interaction in the excitation state. The quenching was mainly attributed to the photoinduced charge transfer from **28** to C_{60}. In CNT (carbon nanotube) composites, similar interaction was confirmed.

Chen et al. also reported composites of **29** with C_{60} and CNT, i.e., a polyimide consisting of perylene and DAF skeletons (Figure 12).[19] The interaction between **29** and the fillers is stronger than the intermolecular interaction between **29** mole-



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31

Figure 13. Structures of epoxy resins **30** and **31**.

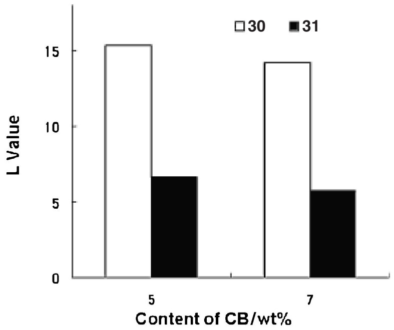
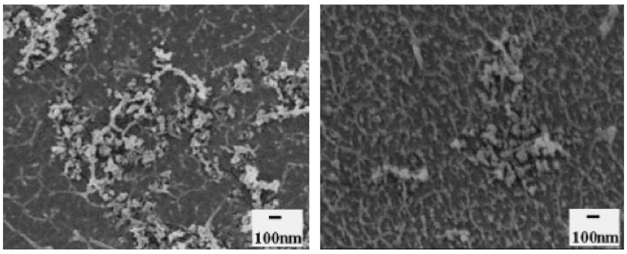


Figure 14. *L* values of the CB composites.



(a) CB/30

(b) CB/31

Figure 15. FE-SEM images of **30** or **31** composites with CB.

cules, and therefore, it is believed that the complex between the large π-conjugated system and the carbon fillers easily causes photoinduced charge transfer.

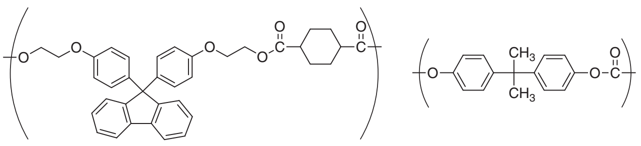
Kawasaki et al. evaluated the properties of the composites of DAF or bisphenol A containing epoxy resins **30** and **31** with carbon black (CB) (Figure 13).[20]

To compare the CB dispersing ability of the two CB/epoxy resin composites, the blackness (L) of the composites was measured (Figure 14), where $L = 0$ and 100 mean completely black and white, respectively. In comparison to the L values of these composite membranes, CB/**31** showed less than half the value of CB/**30**. Thus, the low L value of CB/**31** clearly depends on the good dispersing power of DAF containing epoxy resin **31**.

Furthermore, the results of the reflectance spectrum in visible wavelengths and FE-SEM showed that the blackness of CB/**31** comes from the very fine dispersion of CB in **31** (Figure 15).

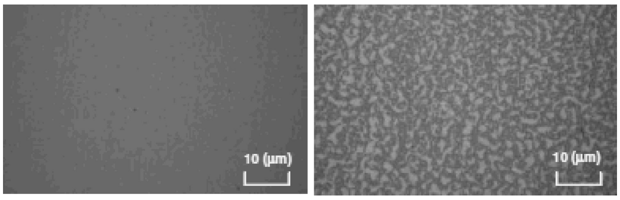
Furthermore, Kawasaki et al. studied the carbon filler-dispersing ability of composites between multiwalled CNTs and **32** using a digital microscope, by comparing with that of PC. The aggregation of CNT was observed in the CNT/PC composite, but not in CNT/**32**. The good CNT dispersing ability of DAF containing polymer **32** was again confirmed (Figure 16).

A structure simulation of DAF and CB was also performed by Kawasaki et al. to clarify the mechanism and the reason for the high CB dispersion ability of DAF containing polymers. Graphene (C96) and 9,9-bis(4-ethoxyphenyl)fluorine (EPF) as the model of CB and DAF containing polymer, respectively, were used in the MM2 calculation as shown in Figure 17. Not only the fluorene moiety but also the aromatic rings at C9 interacted directly with the graphene plane in EPF. Their multivalent and large π-face–face interactions probably make possible the high CB dispersion.



32

PC



(a) CNT/32

(b) CNT/PC

Figure 16. Digital microscope images of CNT containing composite resins.

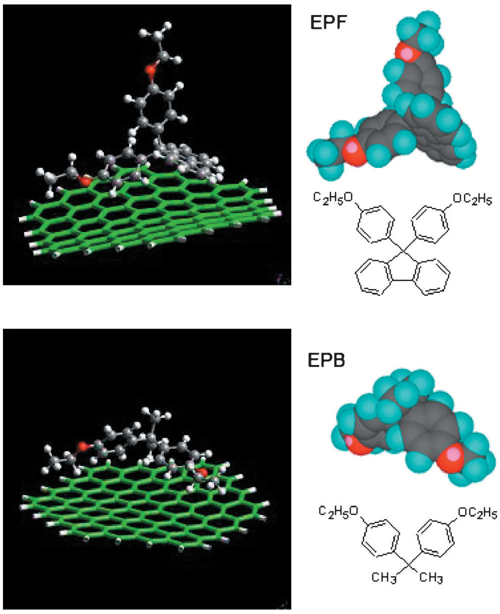


Figure 17. MM2 calculated interaction between model compounds of DAF, bisphenol A, and CB.

Kawasaki et al. prepared a hybrid membrane from DAF diacrylate (**33**, Figure 18) and titanium oxide–silica-sol using photoinduced radical polymerization.[21] A transparent membrane without cracks, obtained by blending more than 20 wt % of **33**, showed high refractive indices from 1.62 to 1.82 depending on the amount of **33** added.

4.2 Polymer Alloy Using DAF Containing Polymers

The DAF containing polymers are generally amorphous and transparent due to the low orientation and high molecular

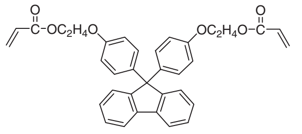


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Figure 18. Structure of **33**.

mobility resulting from the *Cardo* structure. Therefore, its polymer alloys with other polymers are expected to enhance mechanical and optical properties as well as processability.

PC is known as a leading optical resin with a rather high refractive index of 1.58. However, PC has some issues to be addressed such as large birefringence and high melt viscosity making processing difficult. While polymer alloys with poly(ethylene terephthalate) (PET) is suggested to reduce the viscosity, the alloying process requires high temperature causing some coloration. In addition, the birefringence of PET is too large to reduce the birefringence. Thus, Kawasaki et al. examined the preparation of an alloy of PC with DAF containing polyester instead of PET.[16]

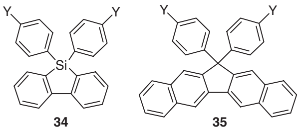
Polymer alloys of PC were obtained with **32** and PET by melt blend. The alloy membrane **32**/PC was a transparent film with single T_g and $\tan\delta_{max}$, suggesting good compatibility of **32** and PC. On the other hand, the PET/PC alloy membrane was not transparent and had a couple of $\tan\delta_{max}$ values, indicating poor compatibility. Furthermore, the refractive index of **32**/PC increases as the concentration of **32** increases, suggesting that the refractive index is tunable. In addition, the birefringence of **32**/PC membrane was much smaller than that of PET/PC: ten times the difference for an alloy of 50 wt % **32** or PET.

The film of **32**/PC showed good drawing properties, which are enhanced as **32** content increases. Furthermore, the large viscosity reduction of PC was confirmed by the addition of **32**, resulting in a drastic improvement in the processability. The solid-state NMR study of a **32**/PC membrane suggested the improvement of the fluidity of PC by the addition of **32** at a molecular level.

◆ 5. New Cardo Monomer

Takata et al. have studied the modification and transformation of the DAF structure for the development of new DAF monomers. The replacement of C9 with silicon afforded a new organic–inorganic hybrid DAF monomer **34**,[22] while the double benzo-annulation of the original DAF structure resulted in the synthesis of an expanded fluorene skeleton **35**[23] (Figure 19). These structural modifications contributed to improvement of the corresponding polymers, i.e., the enhancement of thermal stability and refractive index, especially in **35**-based polyester and polyimide in comparison with those of the DAF.

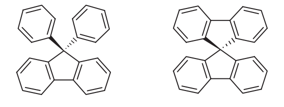
Takata et al. have also investigated an analogous structure of DAF, i.e., 9,9′-spirobifluorene (SBF) to clarify the effect of the spirocyclization of DAF (Figure 20). The structure of SBF is unique enough to be transformed to the corresponding monomers and polymers because a higher refractive index is expected from its chemical structure.[24]



34 **35**

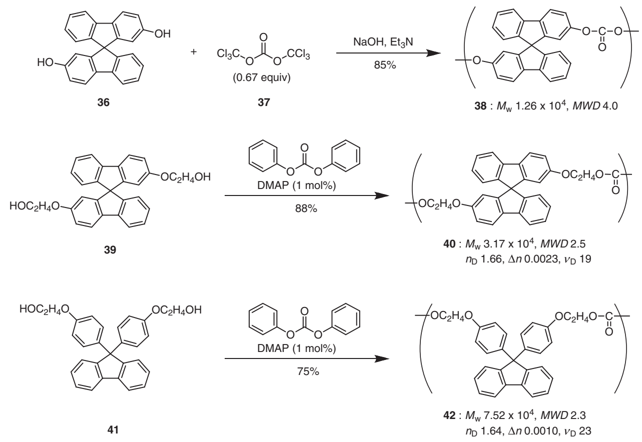
Y = OH, SH, NH$_2$, etc.

Figure 19. New *Cardo* monomers.



9,9-diarylfluorene 9,9′-spirobifluorene

Figure 20. DAF and SBF structures.



Scheme 3. Polymerization of SBF monomers.

Polymers containing the SBF moieties in the main chains have been studied mainly from the view points of materials with gas permeability, electroluminescence, and photoluminescence. However, its optical properties such as the refractive index have never been studied. Takata et al. synthesized a polycarbonate containing the SBF skeleton in the main chain using optically active diphenolic monomer 2,2′-dihydroxy-9,9′-spirobifluorene (**36**) (Scheme 3).[24] Because the polymerizability of **36** was too low to give a polymer of high enough molecular weight to form a self-standing film, probably due to the steric hindrance resulting from the low flexibility around the spiro carbon. Subsequently, Takata et al. designed and synthesized the alkylene spacer-tethered dihydroxy monomer **39**. The monomer showed good polymerizabiliy as expected to afford polymer **40**. Comparing **40** with DAF containing polymer **42**, the refractive index was improved by the modification of DAF to SBF, while the birefringence and Abbe number of **39** were almost as good as those of **42**.[25]

A variety of SBF containing polyesters **43** (Figure 21) are synthesized by Takata et al.[25] All polyesters show high refractive indices, as shown below, almost independent of the aromatic acid structure. In particular, **43** had much lower birefringence values than the corresponding DAF derivatives. Thus, the results suggest the usefulness of the SBF skeleton as an attractive moiety capable of achieving excellent optical properties.

A similar spiro skeleton tethering polymer, spiro(anthracene–fluorene) containing polythiophene **44** (Figure 22) was reported as a hole-transfer material of a photovoltaic cell by Kim et al.[26] They prepared a composite membrane of **44** and porous

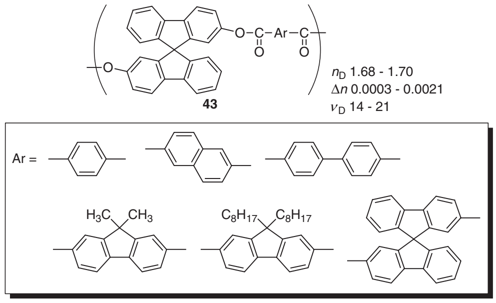


Figure 21. SBF containing polyesters **43**.

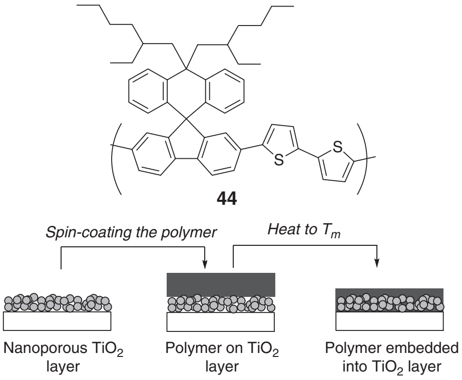
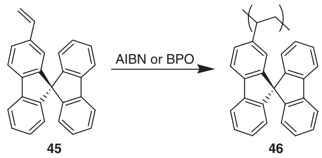


Figure 22. **44** containing polythiophene and composite procedure with titanium oxide.



Scheme 4. Poly(vinylspirobifluorene).

titanium oxide. The photoluminescence of the membrane was quenched by annealing in a composite process, and therefore, the strong donor–acceptor interaction between the spiro(anthracene–fluorene) skeleton and titanium oxide in an excited state was suggested. In the case of **44**, the good dispersing ability of the filler was also confirmed similar to that in DAF polymers.

A vinyl monomer tethering SBF moiety **45** was designed and polymerized to the corresponding polymer **46** (Scheme 4).[27] The vinyl monomer **45** showed good polymerizability in radical polymerization to yield **46** with a sufficiently high molecular weight. The polymer **46** showed not only good thermal stability but also high transparency around visible wavelengths (>90%) and a high refractive index (1.61 at 589 nm). Again, the SBF structure can be regarded as an effective property enhancing moiety upon introduction into both the polymer main chain and side chain.

◆ 6. Concluding Remarks

The authors have discussed the outstanding properties of polymers introduced with 9,9-diarylfluorene (DAF) or 9,9′-spirobifluorene (SBF) moieties into the polymer main chains, and side chain in a limited case, in this review. In particular, these polymers are unique and useful enough to display good transparency, high refractive index, and low birefringence, in addition to high thermal stability and solubility, although they have highly dense aromatics and are composed only of C, H, and O. Furthermore, the excellent filler dispersing power and polymer alloy-forming ability seem remarkably interesting and quite useful. Although a few DAF containing polymers are used practically today, a variety of DAF and SBF containing polymers can be synthesized, holding high potential as future optical materials. By advancing the research activity on this issue, many novel monomers and polymers with prominent properties can be developed, as exemplified in the last part of this review.

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