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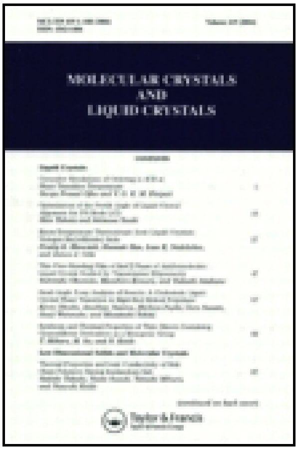

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

Synthesis of Amorphous Molecular Materials with Multiple Azobenzene Units by Palladium-Catalyzed Amination and their Photochromism

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Version of record first published: 24 Sep 2006

To cite this article: A. Honma, T. Kanbara & K. Hasegawa (2000): Synthesis of Amorphous Molecular Materials with Multiple Azobenzene Units by Palladium-Catalyzed Amination and their Photochromism, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 345:1, 125-130

To link to this article: http://dx.doi.org/10.1080/10587250008023906

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Mol. Cryst. and Liq. Cryst., 2000, Vol. 345, pp. 125-130
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Synthesis of Amorphous Molecular Materials with Multiple Azobenzene Units by Palladium-Catalyzed Amination and their Photochromism

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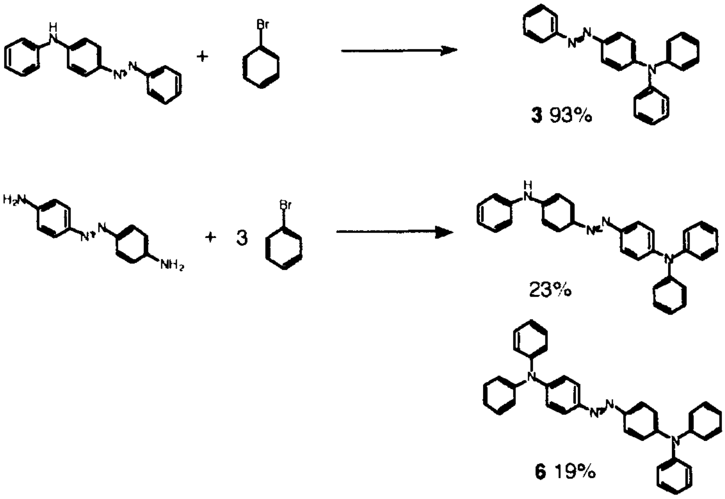
New photochromic amorphous molecules containing core of triphenylamine and three branches of azobenzene were obtained in good yields by Pd-catalyzed amination. High glass temperature (T_g) above 100 °C of these molecules was because of many triphenylamine units and high molecular weight. The stable amorphous films of these molecules could be easily prepared by spin-coated method. The photoinduced and thermal isomerization were observed in the amorphous films and the solutions. The size of the core had no clear effect on rates and activation energy values (E_a) of the cis→trans thermal isomerization in solution.

Keywords: triarylamine; amorphous; isomerization; azobenzene

Triarylamine derivatives are an important class of compounds because they can be building for polyradicals and they form stable amorphous glass with high T_g[1-3]. In particular, the triarylamines have been used as the hole-transport layer in electroluminescence, owing to the advantages of high purity, monodispersion, stability of morphology, and uniformity of the film. Photochromic amorphous glass containing triarylamine and azobenzene units has recently been reported[2, 3], and the photogenerated cis-form in the amorphous film could be considerably stabilized by incorporation of bulky group[3]. The triarylamines have generally been prepared by the Ullmann reaction, but the low yields by this reaction have prevented the preparation of triarylamine dendrimers. Recently, Pd-catalyzed amination have been investigated[4], and many arylamines, polymers, and dendrimers have been prepared in good yields. We have prepared new molecules containing core of triphenylamine units and three branches of azobenzene by the Pd-catalyzed amination.



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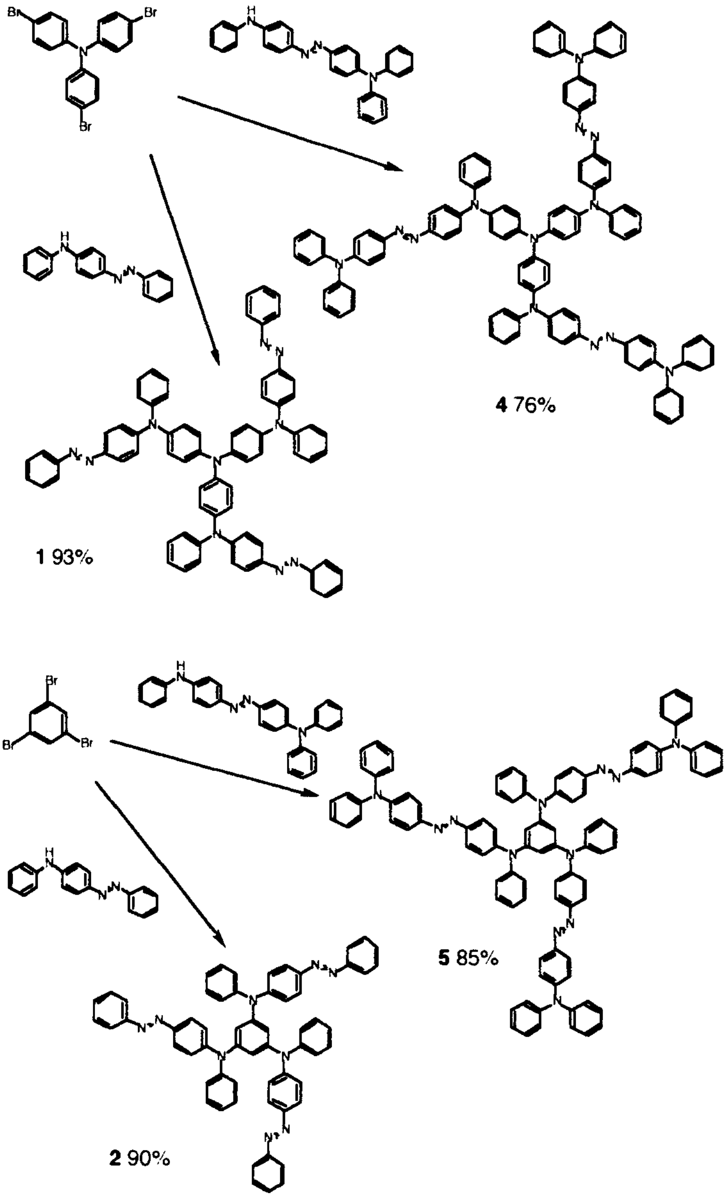

4 76%

1 93%

5 85%

2 90%

SCHEME 1

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Preparation of **1** was carried out by stirring a mixture of tris(4-bromophenyl)amine (241 mg, 0.5 mmol), 4-phenylaminoazobenzene (451 mg, 1.65 mmol), NaO-t-Bu (288 mg, 3 mmol), $Pd_2(dba_3)$ (23 mg, 0.025 mmol), and tri(t-butyl)phosphine (31mg, 0.15 mmol) in toluene (20 mL) at 100 °C for 24 hours under N_2. The mixture was quenched by adding aqueous ammonia and the product was extracted with $CHCl_3$. The product was separated by column chromatography on silica gel ($CHCl_3$) and was recrystallized from methanol (reddish powder). As shown in Scheme 1, **2-6** and 4-diphenylamino-4'-phenylamino-azobenzene were also prepared similarly by the Pd-catalyzed amination. **1, 2, 4,** and **5** were obtained in good yields. Their structures have been confirmed by elemental analysis and FT-IR and NMR spectroscopy.

The molten samples of **1, 2, 4,** and **5** gave amorphous glass by cooling at room temperature. T_g of **1, 2, 4,** and **5** were 118, 100, 144, and 136 °C, respectively. High T_g of **2** would be caused by many triphenylamine units and high molecular weight. T_g of **3** and **6** were not observed above room temperature. The spin-coated film of **6** was crystallized within two days, in contrast, the films of **1-5** were not crystallized even up to two weeks.

The absorption peak of **1** at 430nm in toluene gradually decreases by light irradiation due to the trans→cis photoisomerization of azobenzene units. When the sample of the photostationary state was annealed at 60 °C in the dark, the absorption peak steadily increased to the starting value before irradiation indicating the cis→trans thermal isomerization. Similar changes in the absorption spectra of the solutions and the spin-coated films of **2-6** were also observed.

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TABLE 1 The isomerization of photochromic materials.

Sample	R^*_{sol}	$k_{60}{}^{\dagger}{}_{,sol}$ x 10^3 / s^{-1}	$E_a{}^{¶}{}_{,sol}$ / kcal mol^{-1}	R^*_{film}
1	0.51	0.585	20.0	0.73
2	0.39	0.485	19.1	0.61
3	0.33	0.532	20.7	0.59
4	0.58	11.4	17.8	0.86
5	0.39	7.42	18.2	0.79
6	0.35	8.97	16.3	0.86

*The absorption ratios (*R*) of *photostationary* state to *trans-form*; *R* = A_{pss} / A_{trans}. †The thermal isomerization rates at 60 °C in toluene. ¶The activation energy values (E_a) of the thermal isomerization are evaluated from the slope of the Arrhenius plots.

As shown in Table 1, the cis→trans thermal isomerization of **1-6** in toluene obeyed first-order kinetics, because isomerization of the branches of azobenzene occurred individually. The size of the core had no clear effect on the rates and the E_a. **4-6** with diphenylamino units on 4'-position of azobenzene have smaller E_a and faster rates than those of **1-3** without diphenylamino units, respectively. The smaller E_a and the faster rates might be caused by steric hindrance of diphenylamino units at cis-form.

As described above, several new photochromic amorphous molecules containing core of triarylamine and three branches of azobenzene were obtained in good yields by the Pd-catalyzed amination. The photoinduced and thermal isomerization were observed in the amorphous films and the solutions. Further studies on larger molecules containing many branches of azobenzene are in progress.

Acknowledgments The authors wish to thank Associated Professor K. Ashida and Mr. M. Hara, Hydrogen Isotope Research Center, Toyama University, for their helps to measure DSC and XRD.

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