

Synthesis and Properties of the Vertical Alignment Materials containing Liquid Crystal-like Side Chain

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Abstract

Poly(amic acid) precursors were prepared by mixing various main chain dianhydrides, main chain diamines and side chain diamines. The side chain diamine has an alkylbicyclohexyl group as a side chain. The copolyimide films, produced by casting the poly(amic acids) solution, exhibited the vertical alignment property without the rubbing process in the range of the curing temperature from 90 to 240 for 1h. The thermal and surface properties of the poly(amic acids) depending on the curing temperature was examined.

1. Introduction

The VA technology is based on the homeotropic alignment concept to align the LC molecule vertically on the alignment layer at the field-off state. [1, 2] To obtain the wide and symmetric viewing angle in VA-LCDs, it is necessary to pattern the liquid crystal alignment in multi-domains. It is a good method that the patterning of the pixel electrode to inducing the fringe effect in the electric field. [2] This method makes the manufacturing process more simple and stable because the method does not require the rubbing process. Electro-optical performance of these VA-LCDs is affected by the alignment layers which make uniform alignment state in non-rubbing and non-electric field.

The polyimide for vertically aligning the liquid crystal molecule was developed by the many researchers. [3-7] These polyimides have a structure of a side chain, such as alkyl group, alicyclic group, fluoro group, and etc. In previous works, we synthesized the polyimide containing the alkylcyclohexylbenzyl group. [5]

In this paper, we synthesized polyimides having an alkylbicyclohexyl group as a side chain. The imidization behavior of this poly(amic acids) was investigated by DSC and TGA. While the curing process is ongoing, the imidization ratio and the surface tension were examined.

2. Experimental

2.1 Synthesis of side chain monomer

We synthesized a side chain diamine of 5-(trans-4'-pentylbicyclohexyl-4-yl)-benzene-1, 3-diamine as shown in figure 1. 4-(3, 5-dibromophenyl)-4'-pentylbicyclohexyl-4-ol (4) was coupled by mixing a ketone compound (3) and a 1,3,5-tribromobenzene. [8, 9] 4-(3, 5-Dibromo-phenyl)-4'-pentyl-bicyclohexyl-3-ene (5) dehydrated from a previous compound was converted into an amine compound (6) by the catalytic amination reaction. [10] Finally, two isomers of diamine compounds (7) were synthesized by the catalytic reduction reaction, and then the trans-isomer was purely obtained by the recrystallization. The

chemical structure of the product was identified by ^1H NMR spectroscopy (Bruker Avance 400 Spectroscope) and EI mass spectroscopy. (70eV Hewlett Packard 5972 MSD)

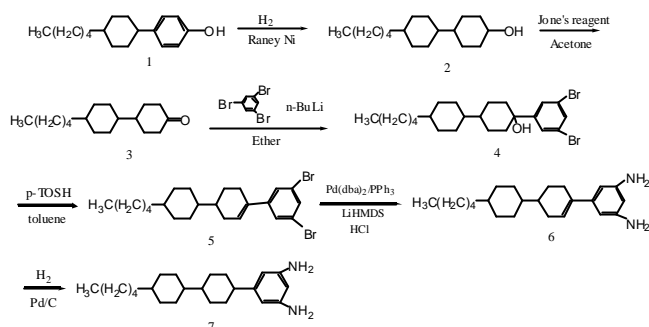


Figure 1. synthetic route of side chain diamine

2.2 Synthesis of Poly(amic acid) and Measurement

Poly(amic acid) precursors were prepared by copolymerization after mixing dianhydrides, main chain diamines and side chain diamines (mole ratio of 3:2:1) in 12 wt% solid concentration of 1-methyl-2-pyrrolidinone in a nitrogen atmosphere as shown in Figure 2. The GPC curves of the synthesized poly(amic acid) was obtained by the Jasco GPC system equipped with the RI detector and the phenogel column in the solution ($\text{LiBr}/\text{DMAC}=1\text{g}/1\text{L}$) at 60 . The average molecular weight of the poly(amic acids) was calculated by using standard materials (PM-1: Easical, Polymer Lab) and the Jasco software. The poly(amic acid) solution was coated on ITO glass substrates. Poly(amic acid) was converted into polyimide by the thermal imidization through pre-curing at 90° for 3min and respective main-curing temperature. The thermal properties of the poly(amic acids) was examined by DSC (Perkin Elmer Diamond DSC) and TGA (Perkin Elmer TGA7) in N_2 atmosphere. The imidization ratio depending on the curing temperature was determined from the FT-IR

measurement. (bomem FT-IR) The Pretilt angle of nematic LC (MJ961213; Merck Co.) was measured with an optical instrument set by applying the crystal rotation method. [11] The contact angles were measured by the sessile drop method using a contact anglemeter (KRÜSS DSA100) with highly pure distilled water and methylene iodide. The surface free energy was calculated by Owens's formula. [12]

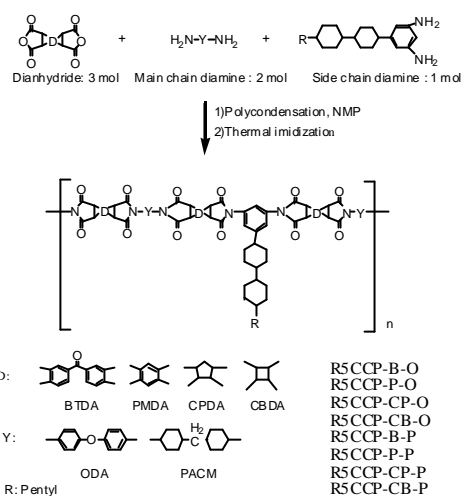


Figure 2. The synthetic route of polyimides

3. Result and Discussion

3.1 Synthesis of Poly(amic acid)

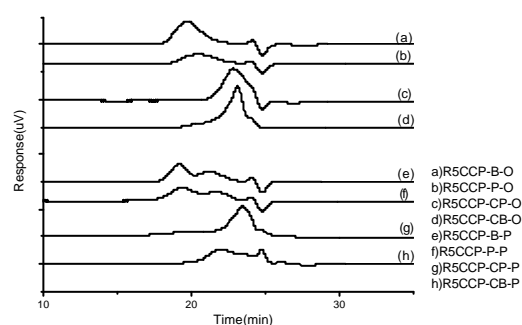


Figure 3. gel permeation chromatograms

The gel permeation chromatograms of the synthesized poly(amic acid) are shown as figure 3. As these results, the molecular weight distributions of poly(amic acid) are mainly affected by the

dianhydride structure. The poly(amic acids) containing the aromatic dianhydride have higher molecular weight distribution than that containing alicyclic dianhydrides (CPDA, CBDA). Although the GPC curves of poly(amic acids) with ODA are mostly consistent with those with PACM, the poly(amic acids) such as R5CCP-B-P and R5CCP-P-P have the GPC curves containing two peaks. When the aromatic dianhydride reacts with two kinds of diamines, such as aromatic and alicyclic structure, these poly(amic acids) have two peaks of GPC with different molecular weight distribution. However, the poly(amic acids) containing the alicyclic dianhydride don't exhibit this result.

3.2 Thermal properties

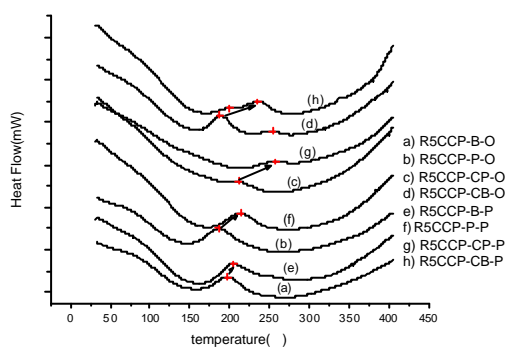


Figure 4. DSC thermograms

The DSC curves of poly(amic acids) are shown as Figure 4, and the thermal properties of these poly(amic acids) by DSC and TGA as table 2. The imidization process of the poly(amic acid) was manifested by DSC, and the endothermic peaks of the DSC thermograms corresponded to the maximum imidization temperature, which is related to the evaporation of water. [13] The maximum imidization temperature and the initial imidization temperature of poly(amic acids) with PACM is higher than that with

ODA. The R5CCP-P-O has the lowest initial imidization temperature. The decomposition temperature of these poly(amic acids) by TGA exhibits more than 400 °C.

Table 2. Thermal properties of poly(amic acids)

Poly (amic acids)	$T_i^{a)}$ (°C)	$T_{Mi}^{a)}$ (°C)	$T_d^{b)}$ (°C)
R5CCP-B-O	158.5 – 275.9	197.9	442.2
R5CCP-P-O	146.6 – 264.1	186.6	468.9
R5CCP-CP-O	198.7 – 257.3	211.5	437.3
R5CCP-CB-O	160.0 – 278.4	187.9, 253.6	432.4
R5CCP-B-P	161.1 – 291.9	204.9	462.6
R5CCP-P-P	169.1 – 274.5	213.2	459.8
R5CCP-CP-P	214.6 – 278.4	257.5	454.7
R5CCP-CB-P	169.5 – 277.9	200.2, 235.0	424.6

^{a)}: measured by DSC in N₂ atmosphere, ^{b)}: measured by TGA in N₂ atmosphere

3.3 Imidization ratio and surface properties

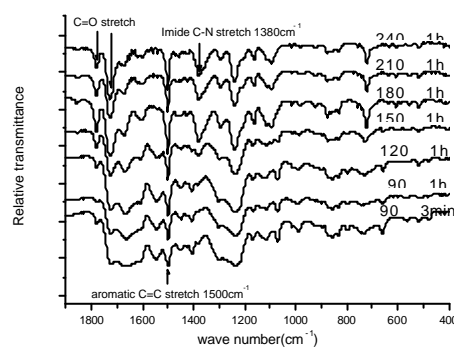


Figure 5. The IR spectrum of the poly(amic acids)

Figure 5 shows the IR spectrum of the poly(amic acids) depending on the curing temperature, and the figure 6 shows the imidization ratio of the poly(amic acids) depending on the curing temperature. The poly(amic acids) with ODA were converted into the polyimides from 90% to 110% at lower temperature than that with PACM. All the poly(amic acids) were

completely converted into the polyimides at 240 for 1h.

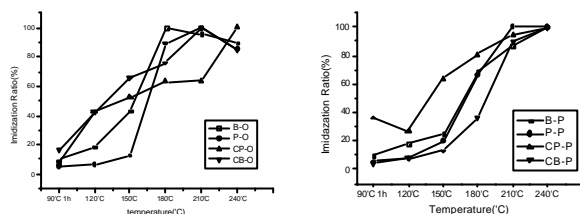


Figure 6. The imidization ratio of poly(amic acids)

Figure 7 shows the surface tension variation depending on the curing temperature. The surface tension of poly(amic acids) is increased with the increase of curing temperature. Especially, in case of the poly(amic acids) with the aromatic dianhydride, the surface tension is less increased than that with an alicyclic dianhydride.

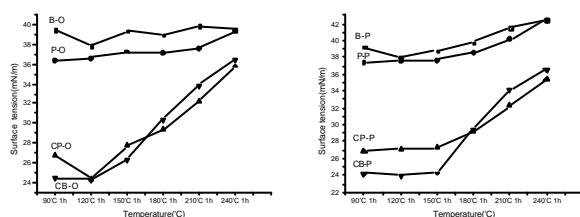


Figure 7. The total surface tension of poly(amic acids)

In observation of alignment state, when the voltage don't applied, the alignment films vertically aligning the liquid crystal exhibit the black image under the crossed polarizer. All the alignment films through the imidization process for various temperature conditions exhibit the vertical alignment state of liquid crystal molecule except for the R5CCP-B-P and R5CCP-P-P at 240 for 1h. These poly(amic acids) have maximum values (R5CCP-B-P;42.41, R5CCP-P-P;42.44) among the surface tension values of the alignment films.

4. Conclusion

We synthesized the vertical aligning materials having

the liquid crystal molecule structure, the alkylbicyclohexyl group, as a side chain. The alignment materials which are the polyimides converted from the poly(amic acids) through the thermal imidization exhibit the vertical aligning properties in the full range of imidization temperature except for R5CCP-B-P and R5CCP-P-P at 240 .

5. Acknowledgements

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6. References

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