Preparation of Novel Alicyclic Polyimide and Application for Liquid Crystal Alignment Layer

Kohei GOTO
Tsukuba Research Laboratory, JSR Corporation,
25 Muyukigaoka, Tsukuba, Ibaraki 305-0084, Japan
TEL:+81-298-56-1217, FAX:+81-56-1726, E-mail: kouhei_gotou@jsr.co.jp

Abstract

Polyimides are important functional polymers for alignment layers in the liquid crystal displays (LCDs). JSR successfully prepared a series of novel polyimides using an alicyclic tetracarboxylic acid dianhydride, 2,3,5-tricarboxy cyclopentyl acetic acid dianhydride (TCAAH). One of the most important feature of these materials is the processability in the fabrication process of the alignment layers at the temperature lower than 180℃. They can therefore be utilized with thin-film-transistor (TFT) and dyed color-filter indispensable for the production of high quality full-color active-matrix (AM) LCDs. Because of the unsymmetrical and bulky structure of the alicyclic unit, these polyimides are soluble in NMP and even in γ-butyrolactone (GBL). The application of GBL avoids the elution of dyestuffs from color-filters. Among these polyimides, the one composed of TCAAH and 4,4'-diaminodiphenylmethane is excellent with respect to its high voltage holding ratio, thereby realizing high quality contrast characteristics. This material has been commercialized under the trade-name "OPTOMER AL 1051", and has been widely employed in TFT-AM-LCDs, in Japan as well as abroad.

What is a liquid crystal alignment layer for LCD?

Alignment layers orient liquid crystal molecules in each picture element cell in order to achieve high quality contrast characteristics of displays. Liquid crystal alignment layers with thickness of 50～70nm are coated on two transparent ITO electrodes, and then rubbed on the surfaces with cloth such as cotton, rayon or nylon along a constant direction. Rigid liquid crystal molecules are filled between the alignment layers of the ITO electrodes. Liquid crystal molecules orient rapidly depending on the applied voltage.

Polyimides for alignment layers

What kind of polymer have been used for alignment layer? Many researchers tried to apply numerous kinds of polymers. Among those polymer candidates, only polyimides have finally been applied. At the initial stage of commercialized LCD, polymers for alignment layer had to have a high thermal decomposition temperature, owing to use inorganic sealing agents for liquid crystal cell. The only commercially available polymer materials with high thermal stability in those days have been polymides. Although the optimal structure of materials for alignment layers is not clarified, it seems that a high glass transition temperature is necessary to keep the alignment of the liquid crystals in the process of the fabrication of LCD cells after rubbing the alignment layer. In addition, from the standpoint of the fabrication processing, it is necessary to provide polymers in solution. Polyimides have two advantage: 1) During the preparation via polyaddition followed by condensation no catalysts are added and no by-products are formed. 2) Broad variations a possible by combination of different monomers, tetracarboxylic dianhydrides and diamines, including copolymerization. This is the reason why polyimides have been applied as microelectronics materials for such a long period.

Subjects of conventional polyimides for alignment layers

At the initial stage of monochrome LCD, polyimides such as pyromellitimide have been used. As such kind of polyimides are not soluble in organic solvents, they are obtained by thermal imidization of poly(amic acid)s, their soluble precursor. Thermal imidization usually requires temperatures of ca. 300～350℃, depending on Tg of the polyimide (1). Such polyimides can only be employed in LCD cells, that are almost entirely made up of inorganic materials.

As the technology changed to full-color LCD, processing temperature was limited to below 180℃ to avoid fade out of the color- filter, which would reduce the contrast imaging, and damage of the TFT. Even when the conventional polyimides imidize at the temperature less than 180℃, the conversion of the imidization is often limited. Chemically unstable, imperfect imidized polyimides, that causes depression of the molecular weight or gradual imidization, yield products with inferior quality.

It became obvious that a high conversion to the imide is essential for a good alignment of liquid crystals (2,3), hence, polyimides with perfect imidization are necessary for the alignment layer.

And also solvent selection used for poly(amic acid) was important on the standpoint of extraction of dyestuff out of color-filter except for NMP, which is the most common solvent for conventional poly(amic acid).

Another important requirement for alignment layer is to have a high voltage holding ratio. This means to keep liquid crystal molecules still between alignment layers while voltage was applied in pulse. When the liquid crystals gradually move with the change of the voltage applied, it leads to the depression of imaging contrast, owing to the change in transmittance of the light. High contrast imaging is essential for high quality TFT-LCDs.

The electrical properties of the liquid crystals play certainly also an important role in imaging of LCDs, because the fillings between the electrodes in LCD cell consists almost entirely of liquid crystals. It has been reported that self-discharging of the LCD cell is influenced by the alignment layer (3). Alignment layers have to reduce leakage current and keep high voltage holding ratio during the cycle period of the frames.

Prospect of soluble polyimides

To avoid thermal imidization at high temperature, soluble polyimides might be processed at low temperature but above the evaporation temperature of the solvent used for processing. The solvents are preferable less polar than dipolar aprotic amide solvents, such as NMP.

Our molecular design for alignment layer is based on improved solubility of polyimides by introduction of unsymmetrical and bulky structures. A suitable polyimide structure is composed of an alicyclic tetracarboxylic dianhydride, 2,3,5-tricarboxy cyclopentyl acetic acid dianhydride (TCAAH), obtained by hydration of dicyclopentadiene, the dimer of cyclopentadiene in the C5 fraction of petroleum, followed by oxidation and dehydration (4), as shown in Fig 1.

A novel series of the polyimides derived from TCAAH has been prepared by polyaddition followed by chemical imidization (5), as shown in Fig.2. These novel polyimides are soluble in dipolar amide solvents, and even cresols and γ-butyrolactone (GBL), expanding the kind of solvents. Among the solvents, GBL is most suitable for coating on ITO with color-filters, since it does not elute dyestuff out (6).

Reducing intermolecular interaction of polyimide in order to increase solubility might cause an decrease of Tg. In alicyclic polyimides derived from TCAAH, Tgs are higher than 350℃, owing to the formation of the continuous rigid rings adjacent to the imide rings. The Tgs are sufficiently high for the thermal treatment condition after rubbing the alignment layers during fabrication of LCD cells.

Electrical characteristics of polyimides

Alignment layers for high quality of displays have to exhibit a high voltage holding ratio as described before. In order to keep a high voltage holding ratio, leakage current at the applied voltage has to be suppressed. Suitable chemical structures have to be electrochemically stable. Conventional aromatic polyimide such as pyromellitimide do not exhibit good voltage holding ratio. It was reported that aromatic polyimides easily underwent electron-migration reaction due to the planar conjugated structure, yielding the low voltage holding ratio (7). Electrochemical stability requires non-conjugated structures. Preferably non-aromatic tetracarboxylic dianhydride are used for the polyimides on the standpoint of planar imide-ring. TCAAH is a candidate as monomer for electrochemical stabile polyimides for alignment layers. According to the report above, aromatic imide-rings contributes to the resonance stability of radical-anion or di-anion during eletrochemical redox process. These experimental results suggest that alicyclic, non-conjugated polyimides have better electrochemical stability than wholly aromatic polyimides.

The contribution of the diamine structure in the polyimide with TCAAH to the voltage holding ratio has been studied in detail; especially the relation of chemical structure with bis-aminophenyl groups (8), and the relationship between polarity and purity (9). Among the diamine candidates, the polyimide composed of TCAAH and 4,4'-diaminodiphenylmethane has a high voltage holding ratio suitable for full-color AM-LCD and can be processed below 180℃.

Some researchers both in Japan and abroad reported that the polyimides for alignment layer composed of TCAAH are suitable for full-color AM-LCD, due to high resistivity (11), excellent transmittance vs applied voltage characteristics (12), small charge accumulation (13), and easy molecular orientation by rubbing (14).

The particular polyimide with TCAAH and 4,4'-diaminodiphenylmethane has been commercialized under the trade-name of "OPTOMER AL 1051" and has been widely employed in the TFT-AM-LCD markets in Japan and abroad. In 1995, the ICHIMURA PRIZE was awarded to JSR for development these materials as contribution to the advancement of LCD industry in Japan.

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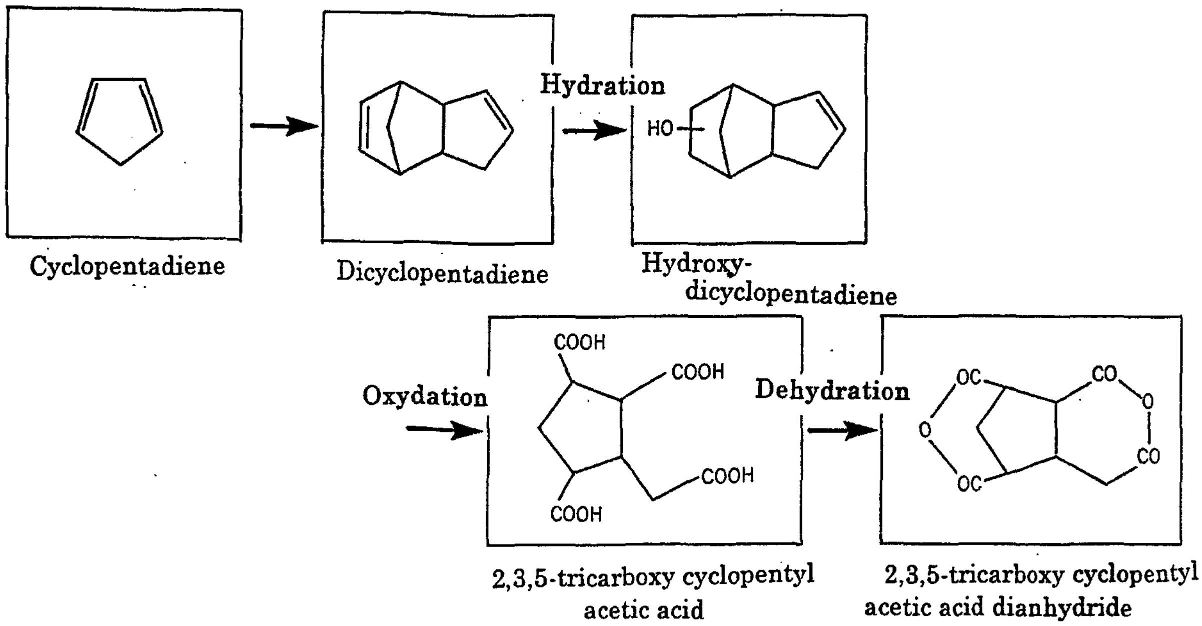

Fig.1 Synthetic scheme of 2,3,5-tricarboxy cyclopentyl acetic acid dianhydride (TCAAH) from dicyclopentadiene

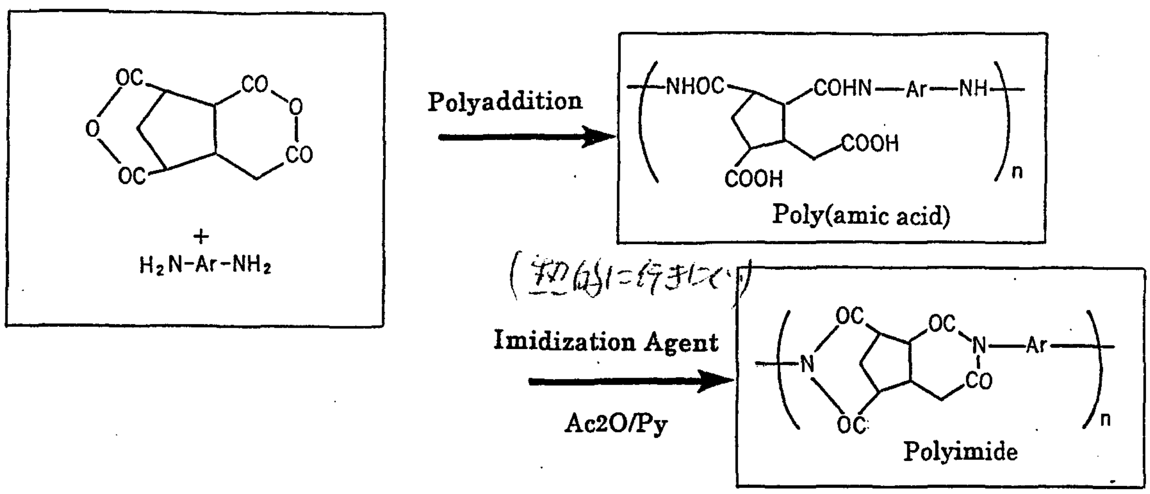

Fig.2 Synthesis of polyimide composed of TCAAH as tetracarboxy dianhydride

solv.
γ butylolactone