

REVIVAL OF NYLON-SALT-TYPE MONOMERS: RAPID SYNTHESIS OF POLYIMIDES FROM NYLON-SALT-TYPE MONOMERS

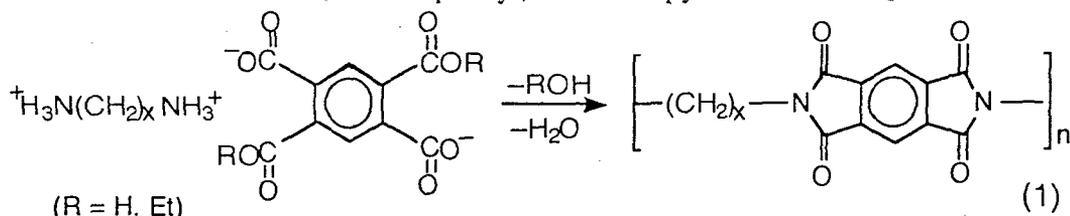
Yoshio Imai

Tokyo Institute of Technology, Meguro-ku, Tokyo 152, Japan

ABSTRACT: This paper reviews our findings on high reactivity of nylon-salt-type monomers composed of both aliphatic and aromatic diamines and aromatic tetracarboxylic acids, which led to the rapid formation of polyimides, and the application of this salt monomer method.

1. Introduction

Aromatic polyimides are known since the early 1960s as high temperature and high performance polymers, and have found many applications mainly in aerospace and electronics industries [1-4]. Aromatic polyimides are generally prepared by a two step procedure, starting from aromatic diamines and tetracarboxylic dianhydrides, while aliphatic polyimides were synthesized in the early 1950s by the melt polycondensation of the nylon-salt-type monomers composed of aliphatic diamines and aromatic tetracarboxylic acids or their diester-diacids (eq.1) [5,6]. Later, in 1967 the synthesis of aromatic polyimide was reported only briefly by the thermal polycondensation of the salt monomer derived from bis(4-aminophenyl) ether and pyromellitic acid [7].



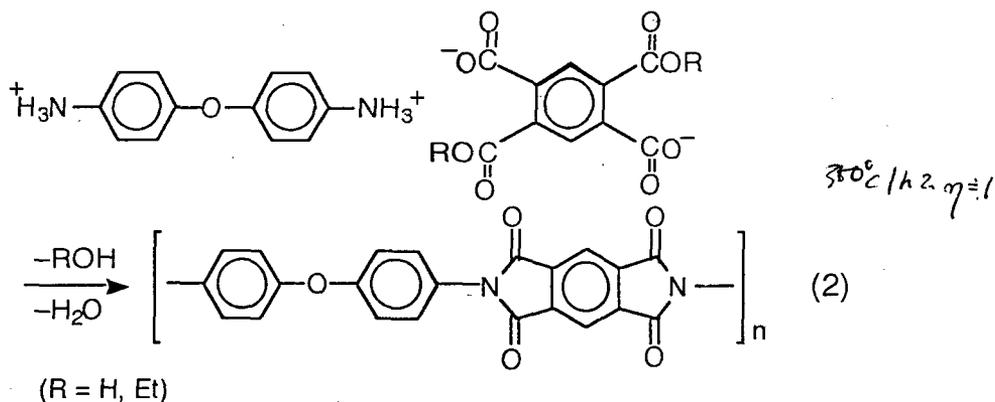
However, no one had recognized the utility of this type of salt monomers for polyimide synthesis, until recently we found that the salt monomers were extremely reactive, producing directly polyimides in a very short reaction time [8-11]. This method can generally be referred to as "salt monomer method". This paper deals with the fundamentals and application of the salt monomer method.

2. Solid-State Thermal Synthesis of Polyimides

A successful example of the polyimide synthesis starting from nylon-salt-type monomers is the solid state polycondensation of the salt monomer 12PMA consisting of dodecamethylenediamine and pyromellitic acid (eq.1, x=12, R=H) [12]. Surprisingly, the polycondensation proceeded rapidly at 240°C, and was almost complete within only 10 min, affording the polyimide having inherent viscosity higher than 1.5 dL/g, despite the fact that the polymerization temperature was far lower than the melting temperature of the polyimide of 305°C.

When the fully aromatic salt monomer ODPMA composed of bis(4-aminophenyl) ether and pyromellitic acid was subjected to solid-state polycondensation at 360°C, the aromatic polyimide having T_g of 410°C was obtained within 1 h in high inherent viscosity over 1.0 dL/g (eq.2, R=H) [13].

Carbon black 1 wt% ? 10⁻⁵ S/cm.



Thus, we found that the aliphatic-aromatic nylon-salt-type monomers as well as aromatic-aromatic were highly reactive, readily producing polyimides by solid-state thermal polycondensation, and successfully developed this finding into a facile and universal synthetic method for polyimides.

3. Microwave-Induced Rapid Synthesis of Polyimides

The application of microwave energy using a domestic microwave oven is a promising methodology for organic synthesis and polymer synthesis as well. In the polymer synthesis field, microwave energy has been utilized for the radical polymerization of vinyl monomers and for the curing reactions of epoxy resins and polyamic acid during the last decade. Nevertheless, there is no report so far on the synthesis of condensation polymers by using microwave energy. We developed a new method for the facile and rapid synthesis of aliphatic polyamides and aliphatic-aromatic polyimides by microwave induced polycondensation [12,14-16].

The microwave assisted polycondensation was carried out simply by heating monomers in the presence of a polar organic medium, which induced effective exothermic molecular friction of the reaction mixtures in a domestic microwave oven. In this system, the presence of a polar solvent having good solubility of the monomers coupled with high boiling point causing high reaction temperature around 300°C was necessary, which facilitated the polycondensation in solution or more commonly in plasticized melt state.

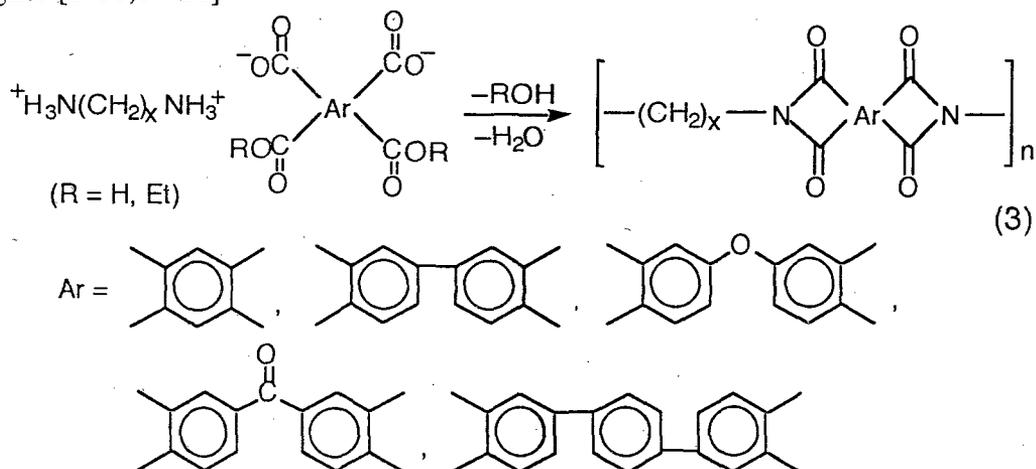
The microwave induced polycondensation giving polyimides was conducted with the nylon-salt-type monomers xPMA or xPME consisting of aliphatic diamines (x: number of methylene unit) and pyromellitic acid PMA or its diester-diacid PME (eq.1) [12]. When 1,3-dimethyl-2-imidazolidone (DMI) or *N*-cyclohexyl-2-pyrrolidone (CHP) was used as the solvent, the polycondensation of the salt monomers xPMA and xPME proceeded very rapidly, and only 2 min of microwave irradiation afforded readily the polyimides with inherent viscosities around 0.7 dL/g or above. The rapid polymer formation is based on efficient internal heating, compared with external heating used for conventional thermal polycondensation.

4. High Pressure Synthesis of Polyimides

High pressure polycondensation leading to condensation polymers such as polybenzimidazopyrrolones, and nylon-11 and -12 has been known for over the past two decades. However, so far, a systematic study of this type of high pressure synthesis has not been reported [11].

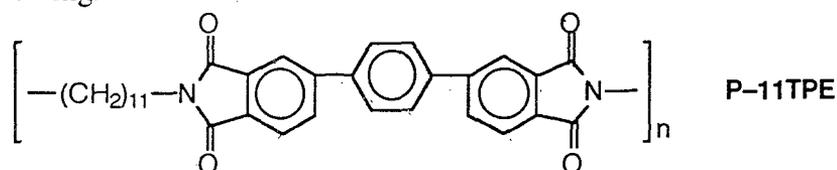
The high pressure synthesis was carried out by using a piston-cylinder type hot-pressing apparatus with use of Teflon capsule as a reaction vessel. We succeeded in the high pressure synthesis of aliphatic-aromatic polyimides directly from the nylon-salt-type monomers composed of aliphatic diamines and aromatic tetracarboxylic acids or their

diester-diacids such as pyromellitic acid, 3,3',4,4'-biphenyltetracarboxylic acid, 4,4'-oxydiphthalic acid, 3,3',4,4'-benzophenonetetracarboxylic acid, and 3,3'',4,4''-terphenyltetracarboxylic acid (eq.3). The high pressure polycondensation of these salt monomers proceeded rapidly in solid state under 200 MPa or above at a temperature between 200 and 340°C, giving the polyimides with inherent viscosities of 0.5 dL/g or higher [8-11,17-20].



It is surprising that the salt monomers directly afforded high molecular weight polyimides within 1 h, despite the facts that the by-product of water (or water and ethanol mixture) produced during the polycondensation was co-existed in the closed reaction vessel and the application of high pressure actually retarded the polycondensation due to restriction of molecular motion of the salt monomer as well as the growing polymer chain ends. An advantage of this process is that the application of high pressure generally produced the polyimides having high crystallinity and high purity, compared with other synthetic methods.

During the course of the high pressure synthesis of the polyimides from terphenyltetracarboxylic acid, we found that some aliphatic terphenyltetracarboxylic acid based polyimides were thermotropic liquid crystalline polymers [18,19]. This is the first example of simple polyimides containing no connecting group in the main chain, that showed thermotropic liquid crystallinity. The typical example is the polyimide P-11TPE derived from undecamethylenediamine and terphenyltetracarboxylic acid diethyl ester. The DSC thermogram of the polyimide exhibited three distinct endothermic peaks upon heating, and again three exothermic peaks upon cooling. Thus, the polyimide was found to form the enantiotropic liquid crystal from 228 to 240°C on heating and from 210 to 169°C on cooling.



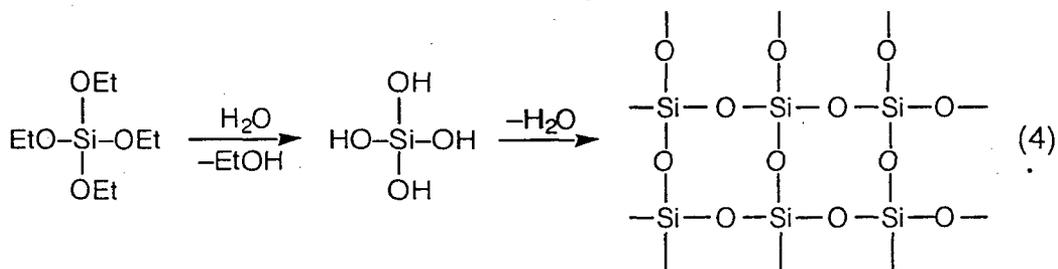
The final goal of the high pressure synthesis is to develop a new method of polymerization hot-pressing for intractable wholly aromatic polyimides directly from the salt monomers. We then attempted the high pressure polycondensation of the salt monomer ODPME consisting of bis(4-aminophenyl) ether and pyromellitic acid diethyl ester, leading to the formation of the aromatic polyimide having high glass transition temperature of 420°C (eq.2, R=Et) [9].

The polycondensation proceeded actually under 220 MPa at 280°C, despite the fact that the reaction temperature was quite lower than the glass transition temperature of the resulting polyimide. However, the inherent viscosity of the high pressure polymerized

polyimide was only about 0.2 dL/g, indicative of low molecular weight. In order to obtain the aromatic polyimide with higher molecular weight, the high pressure polymerized polyimide was subjected to thermal post polycondensation. The viscosity values of the resultant polyimide increased with increasing reaction temperature, reaching to 1.1 dL/g after the post polycondensation at 400°C for 1 h.

5. Preparation of Polyimide-Silica Hybrid Materials

The high pressure polyimide synthesis was applied to develop a new approach for polyimide-silica hybrid materials, where this method was combined with the sol-gel reaction for silica synthesis (eq.4) [21]. Here we selected the polyimide having melting temperature of 310°C derived from the salt monomer 11PMA consisting of nonamethylenediamine and pyromellitic acid (eq.2, x=11, R=H).



An aqueous solution of the salt monomer was mixed with tetramethoxysilane, giving a gel, which was then vacuum-dried forming a precursor powder composed of silica gel and the salt monomer. This was subjected to high pressure polycondensation under 235 MPa at 230°C for 5 h, producing polyimide-silica hybrid molding. By varying the ratio of tetramethoxysilane to the salt monomer, the hybrid materials containing 10 to 100 wt% of silica could be prepared readily.

The hybrid materials having silica content below 50 wt% were composed of polyimide matrix with finely dispersed silica particles, and their hardness values were very close to that of the matrix polyimide. On the other hand, the hybrid materials having silica content over 50 wt% were very hard and tough moldings, and their hardness values increased with increasing silica content. In the latter hybrid materials, silica formed continuous phase with polyimide binder. This is a new type of polyimide-based composite, and may be referred to as polyimide-reinforced silica glass.

6. Conclusion

As can be seen from the above results, the nylon-salt-type monomers composed of both aliphatic and aromatic diamines and aromatic tetracarboxylic acids are highly reactive, giving directly polyimides. Thus, the salt monomer method is very effective for the rapid synthesis of polyimides, and is applicable to practical use for polyimide materials.

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