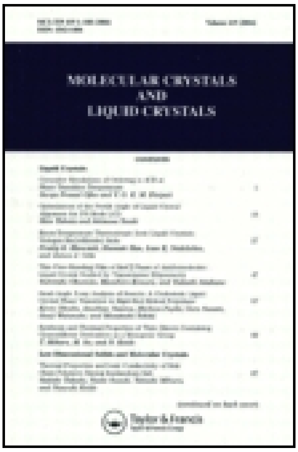

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# Novel Composite Polymers by In-Situ Polymerization of Liquid Crystalline Polymers

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# NOVEL COMPOSITE POLYMERS BY IN-SITU POLYMERIZATION OF LIQUID CRYSTALLINE POLYMERS

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Abstract In-situ polycondensation of terephthaloyl chloride and p-phenylenediamine was carried out by solution or interfacial polycondensation methods in the presence of rubbers such as styrene-butadiene triblock copolymers and acrylonitrile-butadiene randam copolymers so that a novel composite polymers of rubbers and poly(p-phenyleneterephthalamide) was obtained. Mechanical properties of rubbers were greatly improved by the incorporation of rigid rod-like polymers.
In-situ polymerization of N-carboxy methyl-L-glutamate was carried out in solutions of rubbers so that a composite polymer of rubbers and poly(L-glutamate) was obtained. Mechanical properties of rubbers were also greatly improved by the in-situ polymerization, while solution blending of poly(L-glutamte) did not result in the improvement of mechanical properties.

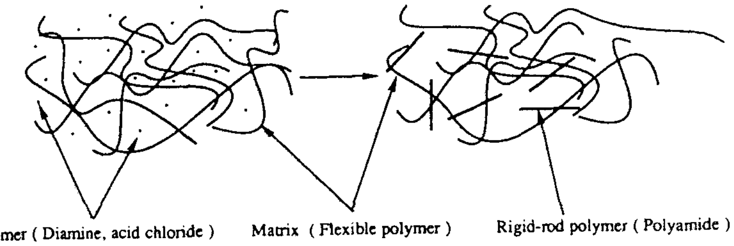
## INTRODUCTION

Liquid crystalline polymers (LCP) usually have high melting points and less solubilities in common organic solvents. Therefore, it is very difficult to blend LCP's with commodity polymers by means of either melt or solution blending methods which result in phase separations of both polymers. Rigid rod-like LCP's show a great improvement effect of mechanical properties when they are incorporated into polymer chains either by block or graft copolymerization and a concept of molecular composites has been attracting many interests. However, synthetic processes of monomers for the copolymerization methods caused problems in terms of preparation of molecular composites.

It was previously proposed by my group[1,2] that in-situ polymerization of monomers which can form LCP's, within solu-

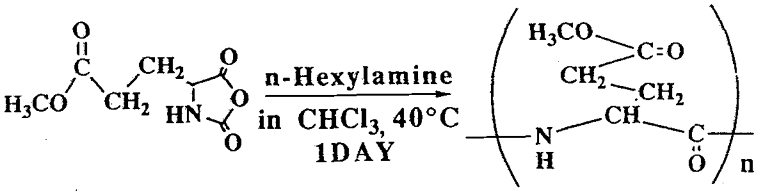
solutions of commodity polymers led to so-called"micro-composites" which resulted in a great improvement of mechanical properties owing to the well-dispersed fine particles of LCP's within the matrix polymers. For instance, p-hydroxybenzoic acid could be polymerized in dichloroethane solutions of sytrene-butadiene triblock copolymer (SBR) by means of a direct polycondensation method so that fine particles of poly(p-hydroxybenzoate) were well dispersed in SBR to achieve a great improvement of tensile strength and modulus of SBR.

The in-situ polymerization method can be expanded to interfacial or solution polycondensation in order to disperse fine particles of polyaramide in SBR, which is illustrated as shwon below:



The in-situ formation of polyaramide in SBR is expected to improve mechanical properties of SBR in terms of tensile strength and modulus at elevated temperatures.

Poly(L-glutamate) which forms helix in solid phase is known as a liquid crystalline polymers in melt or in solutions. Poly(L-gultamate) can be obtained by a ring-opening polymerization of N-carboxy-L-glutamate (L-glutamate NCA) in the presence of amine under mild conditions.

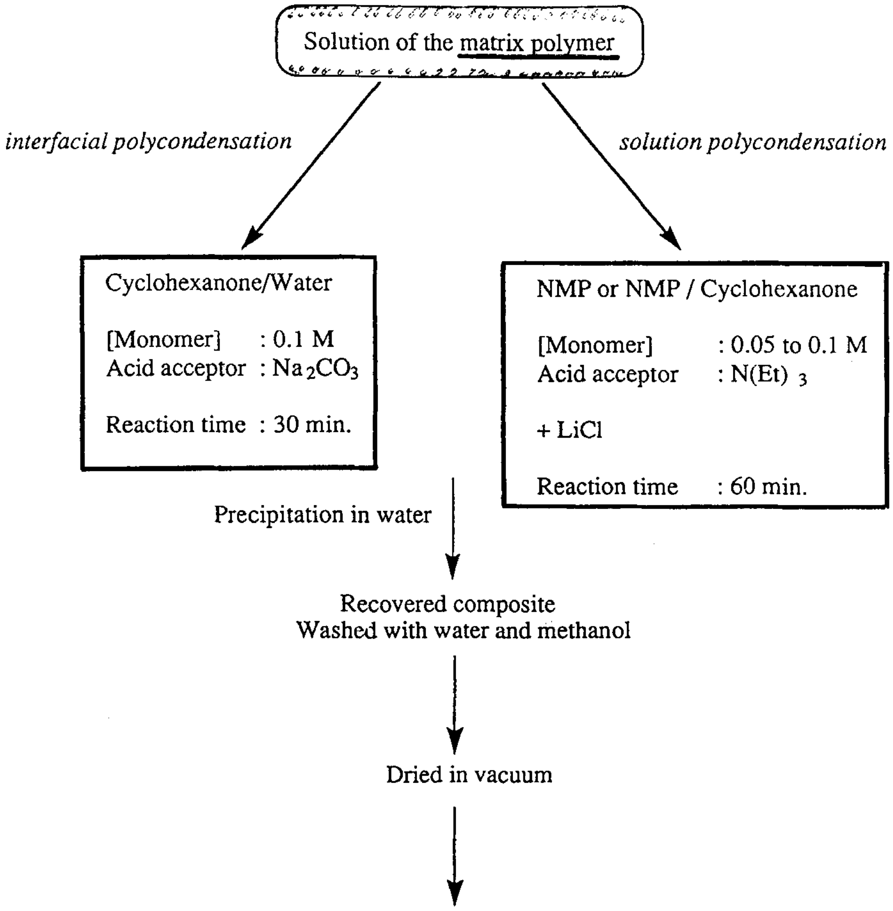


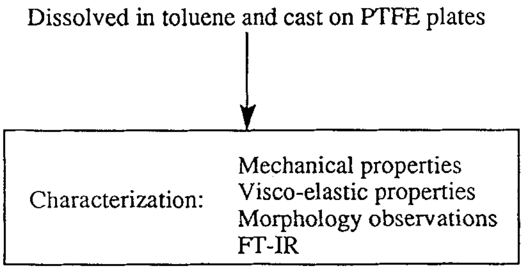
Therefore, methyl-L-glutamate NCA was polymerized in-situ in rubber solutions so that a microcomposite of rubber and poly(L-glutamate) was obtained. Since common solvents for rubber and poly(L-glutamate) are available,solution blending method was also applied to compare with the in-situ method in terms of improvements of mechanical properties.

## EXPERIMENTAL METHODS

### In-situ Fromation of Polyaramide

Interfacial or solution polycondensation of terephthaloyl chloride with p-phenylenediamine was carried out in the presence of styrene-butadiene triblock copolymer (S26) which contained 26 mol% of styrene units, as shown below:





In-situ Formation of Poly(L-glutamate)

Methyl-L-glutamate NCA was polymerized in chloroform which contained elastomers, in the presence of n-hexylamine as an initiator. Three types of elastomers were used as matrix polymers: SBR(S40), hydrogenated SBR(HS20), and hydrogenated styrene-butadiene block copolymer containing 1 wt% of maleic anhydride (SEM20). Each number indicated contents of styrene units in the copolymers. The polymerization continued at 30-35°C for 6 hr with stirring and polymers were recovered by pouring into excess acetone, followed by filtration and drying.

Solution blending of poly(L-glutamate) with matrix polymers was carried out in chloroform solution and films were obtained by evaporating chloroform on a Teflon sheet.

## RESULTS AND DISCUSSION

### In-situ Formation of Polyaramide

Table I indicates results of the in-situ formation of poly (p-phenylene terephthalamide)(PPTA) in S26 or NBR. Two methods resulted in a difference in solution viscosities of PPTA. The reason might be ascribed to the reaction phases which were heterogeneous in the interfacial polycondensation method, while almost homogeneous in the solution method. Decreasing amount of monomers resulted in decreases of both yields and solution viscosities of PPTA, which happened even in the absence of the marix polymers.

Note that the reaction speed did not change at all, although the polycondensation reaction was carried out in highly viscous solutions.

Table I. Experimental data for interfacial and solution in-situ polycondensations

| composition (feet wt %) | [matrix] (wt % in solvent) | [monomer] (M) | yield (%) | $\eta_{sp}/c$ [a] (dL/g) | PPTA content [b] (wt %) |
|---|---|---|---|---|---|
| | | Interfacial polycondensation | | | |
| S26/PPTA | | | | | |
| 0/100 | | 0.1 | 100 | 0.48 | |
| 70/30 | 6.7 | 0.1 | 90 | 0.39 | 27 |
| 80/20 | 9.8 | 0.1 | 79 | 0.32 | 17 |
| 90/10 | 11.4 | 0.1 | 66 | 0.37 | 9 |
| NBR/PPTA | | | | | |
| 70/30 | 5.6 | 0.1 | 98 | | 30 |
| 80/20 | 9.5 | 0.1 | 95 | | 19 |
| 90/10 | 12.9 | 0.1 | 81 | | 8 |
| | | Solution polycondensation | | | |
| S26/PPTA | | | | | |
| 0/100 | | 0.10 | 97 | 3.97 | |
| 70/30 | 5.6 | 0.05 | 98 | 2.40 | 27 |
| 80/20 | 6.3 | 0.07 | 91 | 1.60 | 18 |
| 90/10 | 10.7 | 0.05 | 86 | 1.43 | 8 |
| NBR/PPTA | | | | | |
| 70/30 | 3.7 | 0.10 | 98 | | 29 |
| 80/20 | 9.5 | 0.10 | 83 | | 17 |
| 90/10 | 10.3 | 0.05 | 47 | | 5 |

[a] Reduced viscosity measured, after extraction, in $H_2SO_4$ at 30°C at a concentration of 0.5 g/dL.
[b] Measured by elemental analysis.

Table II summerizes results of mechanical properties of the cast films. Fig.1 indicates mechanical properties as a function of PPTA contents in the composite films. Increases on Young's modulus were observed with increasing contents of PPTA, presumably owing to the fine dispersion of rigid rod-like PPTA in the matrix polymers. Tensile strength of interfacially obtained composites remained about the same regardless of the amount of PPTA, whereas a noticeable decrease was observed for solution method. Both types of the composites indicated a decrease in elongation, but it was more pronounced for the solution method.

To explain the differences in mechanical properties by the in-situ methods, fructure surfaces of the composites were observed under electron microscope (SEM). It was oberved that a large aggregate of PPTA was formed by the solution

Table I I Mechanical properties of the matrix polymers and composites

| | E(MPa) | $\sigma_{200\%}$ (MPa) | $\sigma_b$(MPa) | $\epsilon_b$(%) |
|---|---|---|---|---|
| PPTA/S26 | | | | |
| 0/100 | 33.0 | 2.2 | 18.4 | 1150 |
| 10/90 | 90.0 (90.2) [a] | 6.3 (5.2) | 14.5 (19.5) | 700 (963) |
| 90/80 | 170.0 (131.0) | 13.7 (7.5) | 16.0 (19.8) | 330 (762) |
| 30/70 | 60.0 (195.2) | (8.2) | 2.1 (18.6) | 17 (774) |
| | | σY(MPa) | | |
| PPTA/S44 | | | | |
| 0/100 | 266.2 | 7.4 | 29.8 | 1070 |
| 20/80 | 348.0 | 14.5 | 18.3 | 540 |
| 30/70 | 370.0 | 14.4 | 12.2 | 125 |
| PPTA/NBR | | | | |
| 0/100 | 0.9 | | 0.16 | 1800 |
| 20/80 | 81.0 (8.7) | | 3.4 (0.7) | 112 (510) |
| 30/70 | (69.0) | | (2.3) | (300) |

[a] Values in parentheses are for interfacial method. E, Young's modulus; $\sigma_{200\%}$, tensile strength at 200% of elongation; σY, tensile strength at yield; $\sigma_b$, tensile strength at break; $\epsilon_b$, elongation at break.

method in comparison to the interfacial method. The differences in the aggregate sizes may related with the mechanical properties of the composite films. Fig. 2 indicates SEM micrographs of fracture surface of the composite derived from S26 and PPTA (90/10).

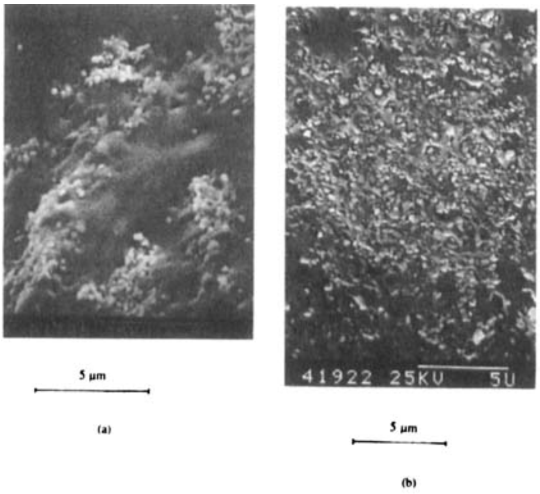


**Figure 2** SEM micrographs of fracture surface of composites of S26 and PPTA (90/10) synthesized by solution (a) and interfacial (b) polycondensation methods.

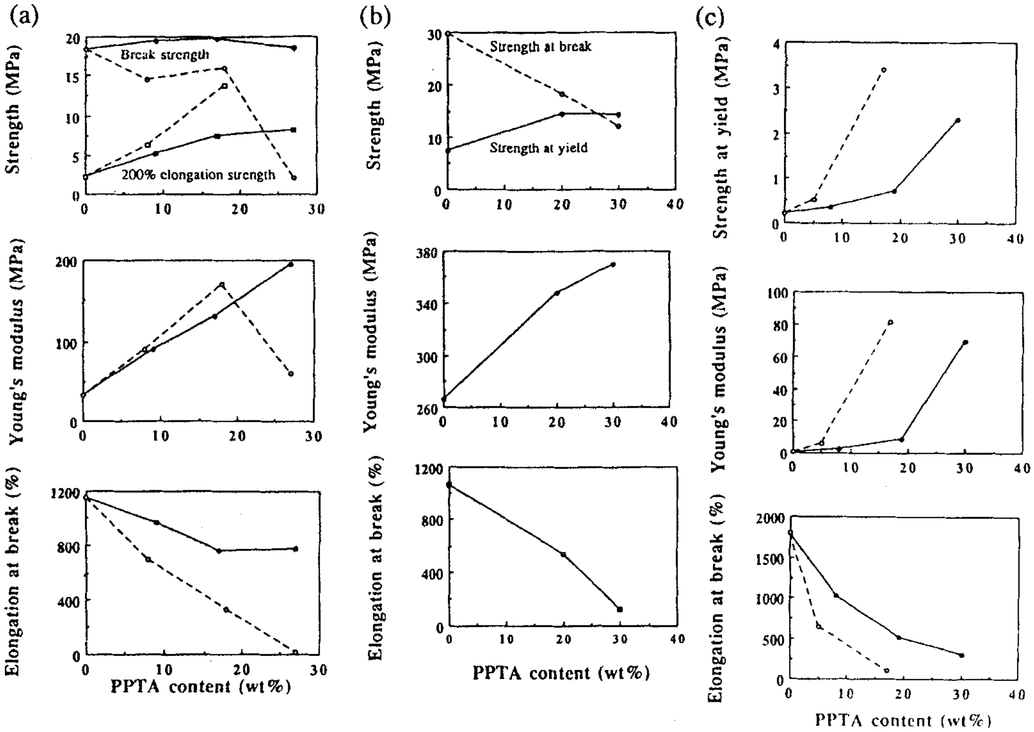
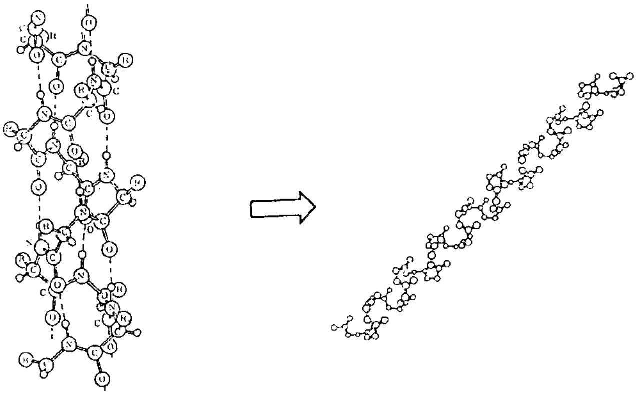


Fig. 1 Mechanical properties of the composites.
(a) S26 synthesized by solution (- - -) and interfacial (——) polycondensation methods.
(b) S44 synthesized by interfacial method.
(c) NBR synthesized by solution (- - -) and interfacial (——) polycondensation methods.

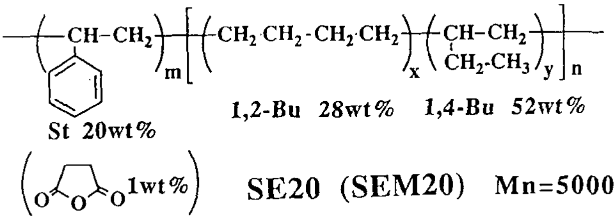
Thus, polyaramide was successfully obtained in-situ in elastmeric materials by both interfacial and solution polycondensation methods under mild conditions. The reinforcing effect of the composite materials was strongly dependent on the particle sizes of PPTA in the matrix polymers. Perhaps, the particle sizes of the in-situ formed PPTA might be ascribed to the changes of monomer cluster which was locally formed in the matrix polymer solutions.

## In-situ Formation of Poly(L-glutamate)

Poly(L-gluatmate) which had a helical structure, was obtained in-situ in solutions of elastomeric materials. It is strongly expected that the helix of poly(methyl-L-glutamate) (PMLG) might have a reinforcement effect of the elastmers.



Both blending and the in-situ methods were applied to SE 20 and SEM20 of which structures are shown as follows:



Sample codes for both blending and the in-situ methods are summarized in Table III.

Table III Sample codes

| Sample Code | Preperation method | PMLG content wt% |
|---|---|---|
| SE20-15B | Blend | 15 |
| SEM20-5B | Blend | 5 |
| SEM20-10B | Blend | 10 |
| SEM20-15B | Blend | 15 |
| SEM20-20B | Blend | 20 |
| SEM20-5 | *in situ* | 5 |
| SEM20-10 | *in situ* | 10 |
| SEM20-15 | *in situ* | 15 |
| SEM20-20 | *in situ* | 20 |

Fig. 3 indicates mechanical properties of the composite films which were obtained by blending and the in-situ methods in terms of tensile strength and modulus.
It is clearly seen in Fig. 3 that mechanical properties of the composite films obtained by the in-situ methods were greatly improved both for tensile strength and modulus in

comparison with blending method.

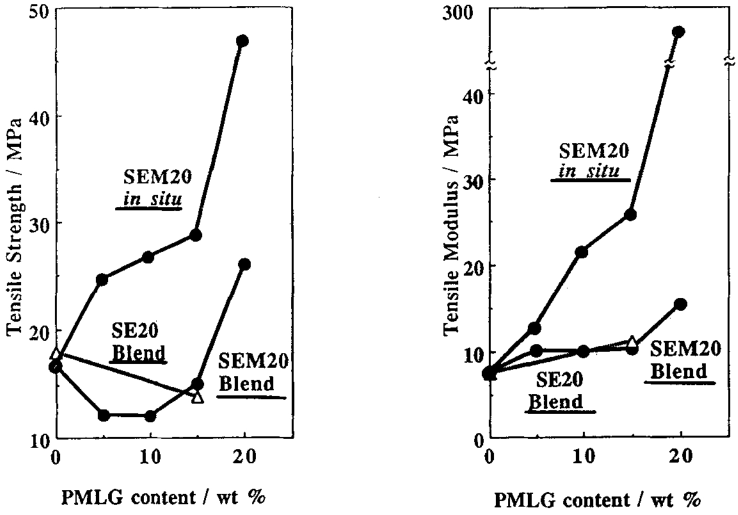


Fig. 3 Mechanical properties of composite films as functions of PMLG contents

Fig. 4 indicates elongations of the composite films. No significant changes of elongations were observed. Normally, elongations of the films decreased significantly when rigid particles were dispersed in polymers, as can be seen in previous chapter for PPTA. Presumably, PMLG might form a hydrogen bonding with maleic anhydride units in SEM20, so that a good compatibility between PMLG and SEM20 was achieved to maintain elongations of the composite films. Morphologies of fine particles of PMLG were observed under scanning electron microscope in order to verify the differences in mechanical properties by the blend and the in-situ methods. Fig. 5 indicates pictures observed under cross-polarized optical microscope. It is clearly seen in Fig. 5 that a large aggregate of PMLG was observed for the blend method, while a finely disperion of PMLG particles was obtained for the in-situ method. This dispersion difference of particle sizes of PMLG caused the difference in mechanical properties of the composite materials.
The dispersion of PMLG in matrix polymers might be caused by a cluster formation of monomer in matrix polymer solution.

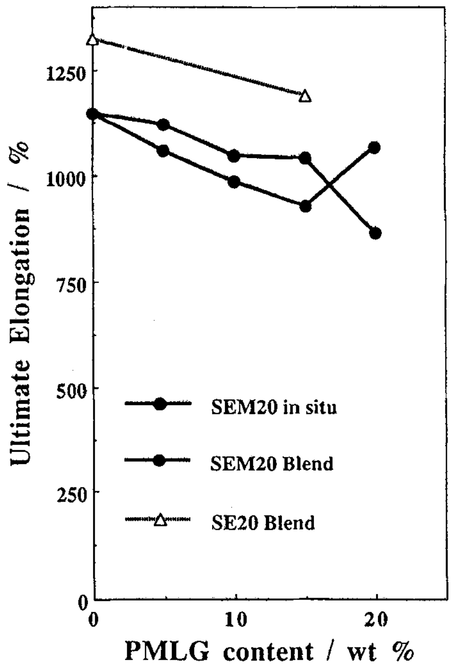


Fig. 4 Elongation of the composite films

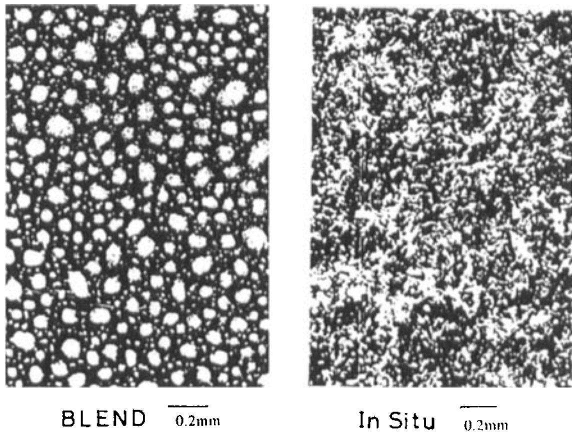


Fig. 5 PMLG pictures observed under cross-polarized optical microscope

## CONCLUSION

In-situ formation of liquid crystalline polymers was carried out for both polyaramide and PMLG in order to improve mechanical properties by the incorporation of these rigid rod-like poymers in matrix polymers. The in-situ method was much superior to the solution blending method because of the finely dispersed particles of LCP in matrix polymers. The in-situ method can provide the reinforcement of mechanical properties of any commodity polymers.

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