

# STUDY ON METHANOLYSIS STABILITY OF OPTICALLY ACTIVE COPOLYMERS OF TRIPHENYLMETHYL METHACRYLATE AND METHYL METHACRYLATE

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## ABSTRACT

The methanolysis of poly(triphenylmethyl methacrylate) (PTrMA) and its copolymers P(TrMA-co-MMA), P(TrMA-b-MMA) has been studied in the presence of anhydrous methanol at 40°C by electroconductometric method. It has been found that the methanolysis stability can be obviously improved for the copolymer, especially, the random copolymer, P(TrMA-co-MMA).

## INTRODUCTION

Optically active poly(triphenylmethyl methacrylate) (PTrMA) with a single-sense-helix is particularly attractive<sup>[1-3]</sup> since PTrMA can be used as a chiral stationary phase in high performance liquid chromatography (HPLC) for direct resolution of racemic compounds<sup>[4,5]</sup>. It was reported that more than 200 racemic compounds including hydrocarbons, esters, amides, and alcohols have been resolved. Most of them are stereochemically attractive and yet they are difficult to be resolved by other methods. As eluents, polar solvent as methanol is more efficient than nonpolar solvent, such as hexane. However, when methanol is used as the eluent the ester groups of PTrMA are slowly solvolyzed to form methyl triphenylmethyl ether<sup>[6]</sup>. Therefore, the drawback of this polymer is its chemical instability during prolonged use. Due to the splitting of triphenylmethyl group the helicity is destroyed and therefore, the ability to the resolution of racemic compounds is lost. In order to improve this defect, Okamoto et al.<sup>[7,8]</sup> have investigated some new PTrMA's with electron-withdrawing substituents on phenyl ring, e.g., meta- and para-chlorosubstituted groups. The obtained polymers show a longer life-time since the mesomeric stabilization within the

triphenylmethyl cation is reduced. Wulff et al.<sup>[9]</sup> also reported a new monomer,  $\alpha$ -(triphenyloxymethyl) acrylonitrile, based on the similarity to the structure of PTrMA, forming single-sense helical polymer with even higher methanolysis stability. But the results of the ability of racemic resolution on this new polymer has not been reported. The monomer with an electron-deficient group, such as nitrile and ether linkage which are relatively stable with respect to acids, bases, reduction and oxidation.

In this paper, we have introduced, MMA is introduced into the backbone of PTrMA. The obtained copolymer, P(TrMA<sub>1</sub>co-MMA) possesses not only highly optical activity<sup>[3]</sup> but also better stability of methanolysis than that of its homopolymer, PTrMA.

## EXPERIMENTAL

The synthesis of PTrMA and its copolymers has been reported elsewhere<sup>[3]</sup>. The methanolysis of the polymer (particle diameter: 50—80 $\mu$ ) which was dispersed in 2.7 mmol/100ml of anhydrous methanol was carried out at 40°C in a closed vessel by using electroconductive method (DDS-11 A model conductometer, conductivity cell constant 0.99)

## RESULTS AND DISCUSSION

It is considered that the methanolysis is not the same as the usual transesterification but proceeds with disruption of the triphenyl-oxygen bond and produces mainly methacrylic acid (MAA) and methyl triphenylmethyl ether<sup>[10]</sup>. Therefore, the electrostatic potential produced in methanolysis process would be increasing with the degree of conversion and can be determined by conductometric method. The relationship between conductometric value (conductivity) and the time for methanolysis of these polymers is shown in Fig. 1.

The polymeric particles suspended in methanol would swell initially due to the penetration of methanol molecules into the polymeric particles. The methanolysis might occur at the interface and proceeds successively along the polymer chain and produces the pendant of carboxyl groups on the helical backbone (Scheme 1).

The methanolysis of the side ester group of PTrMA could be happened with three possibilities<sup>[10]</sup>. The helix to coil transition would be caused by the elimination of the Ph<sub>3</sub> C-oxygen groups to certain extent<sup>[11]</sup>. In our condition the most possible one is that the methanolysis occurs randomly along the helix chain. Once the carboxyl

groups are formed, they could act as acidic catalyst to accelerate the cleavage of

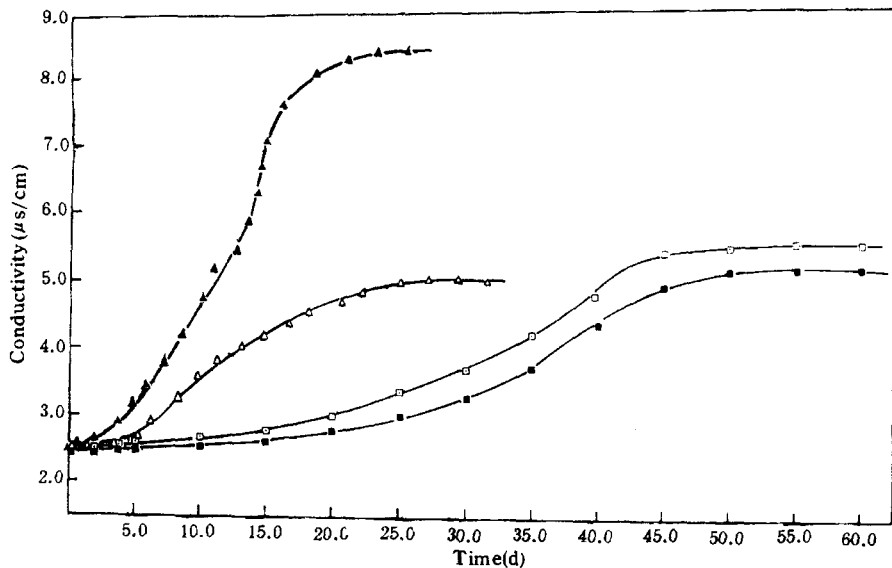
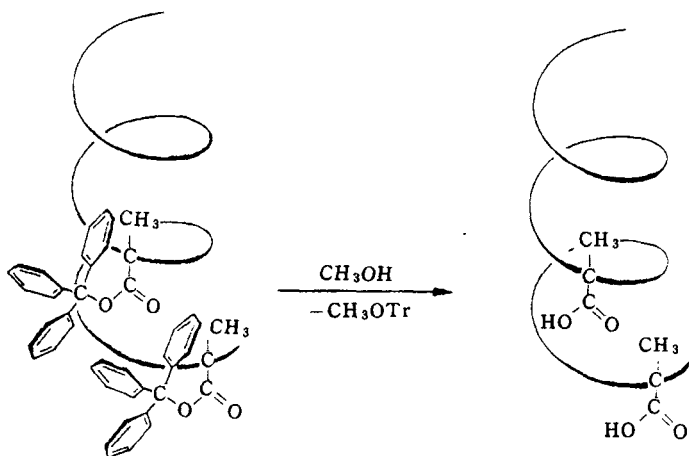


Fig. 1 The relationship between conductometric values and the time of the methanolysis ( $\text{CH}_3\text{OH}$ :  $2.5\mu\text{s}/\text{cm}$ )  $\blacktriangle$  PTrMA;  $\triangle$  P(TrMA-*b*-MMA) (TrMA: 38.2mol%);  $\square$  P(TrMA-co-MMA) (TrMA: 80.0mol%);  $\blacksquare$  P(TrMA-co-MMA) (TrMA: 61.2mol%)



Scheme 1 The methanolysis of PTrMA having helical chain

neighboring  $\text{Ph}_3\text{C}$ -oxygen bond in some degree, meanwhile following the performance of methanolysis. The polymeric particles were gradually dissolved into the solution. The random methanolysis occurs more easily in the solution and takes place accelerated phenomenon. The accelerated methanolysis could directly cause the

conductometric value (conductivity) to increase with the time. The periods of the initial acceleration are about 2.5, 17 and 29 days for PTrMA, P(TrMA-*b*-MMA) and P(TrMA-*co*-MMA), respectively (Figure 1). The methanolysis of random copolymers based on TrMA and MMA seems quite different from that of PTrMA. It could be considered that the MMA units which exist in the helical chain can not be methanolysed in this condition and would prevent the acidic catalysis of the neighboring carboxyl groups formed from the methanolysis of the side ester groups of TrMA units. Therefore, in this case the acceleration of the methanolysis is not obvious. In the block copolymer, P(TrMA-*b*-MMA), the copolymer contains PMMA unit with longer segment which is insoluble in methanol. In fact, the methanolysis of the side ester groups of PTrMA segment is carried out at heterogeneity phase and a homogeneous solution can not be obtained finally when the methanolysis is completed. This heterogeneous methanolysis shows a relatively lower speed and insolubility of methanolysis product of the block copolymer also limits the formation of the protons from methacrylic acid (MAA). It is the reason why the conductometric value (conductivity) would be small.

Optically active PTrMA and P(TrMA-*co*-MMA) have remarkable chiral recognition ability for various racemic compounds containing aromatic groups by using methanol as an eluent (Table 1.).

**Table 1** Chromatographic resolution of racemates on the polymer-coated silica gel column\*

| Chiral stationary phase                   | Racemate | $k'_1$ | $\alpha$ | $R_s$ |
|-------------------------------------------|----------|--------|----------|-------|
| PTrMA                                     | HB       | 0.68   | 1.70     | 1.00  |
|                                           | PBRP     | 2.06   | 1.64     | 1.31  |
| P(TrMA- <i>co</i> -MMA) (TrMA: 80.0 mol%) | HB       | 2.47   | 1.69     | 1.16  |
|                                           | PBRP     | 4.20   | 1.75     | 1.75  |

\* Operating conditions: Column: 100×4.7mm (I.D.), Absorbance monitor D, 254nm, Temp.: 15°C, Eluent: CH<sub>3</sub>OH, Flow rate: 1.0ml/min. HB: (+)-2,2'-dihydroxy-1, 1'-bi-naphthyl, PBRP: (+) -2-phenylbutyrophenone.  $k'_1$ ,  $\alpha$  and  $R_s$ : represent capacity factor, separation factor and resolution factor, respectively

The copolymer P(TrMA-*co*-MMA) possesses improved resistance toward methanolysis. Meanwhile its resolution ability for some racemic compounds is comparable to that of PTrMA. It seems possible to improve the methanolysis stability of PTrMA used as stationary phase by modification through the copolymerization with MMA.

#### Keywords:

Methanolysis; Stability; Optical activity; Poly(triphenylmethyl methacrylate)

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