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## Novel cyclophosphazene monomers and their polymerization behavior

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## Chapter 4

# NOVEL OLEFIN-SUBSTITUTED CHLOROCYCLOTRIPHOSPHAZENES: RADICAL POLYMERIZATION BEHAVIOR

### 4.1 Abstract

The reactivity of the phosphazene containing monomers (STP, VAcP and PP) in radical polymerization reactions has been investigated. The monomer STP could be homo- and copolymerized with MMA and styrene. The copolymerization reactivity ratios for the STP/MMA system were measured. The  $r_1$  (= reactivity of STP) and  $r_2$  (= reactivity of MMA) are 0.21 and 0.48, respectively. The reactivity of STP resembles that of styrene demonstrating the effectiveness of the benzyl group as an electronic and steric spacer between the double bond and phosphazene ring. The monomer VAcP could not be homopolymerized, but was successfully copolymerized. With MMA very low amounts of VAcP were incorporated, but with styrene a maximum incorporation of 20 mol% of phosphazene monomer was achieved with 35 mol% of VAcP in the feed. With higher phosphazene contents in the feed no polymerization was observed. The reactivity of PP resembles that of VAcP. A maximum incorporation of 18 mol% with 61 mol% of PP in the feed was obtained.

## 4.2 Introduction

The synthesis of inorganic-organic polymers is of considerable interest because in this way the advantageous properties of the inorganic component is transferred to the traditional organic polymer. A successful route towards these materials has been offered by the use of chlorocyclophosphazenes substituted with an olefinic group [1-3]. When polymerized with a common organic monomer as styrene or methyl methacrylate, polymers are obtained with the phosphazene ring as a ligand on the organic main chain.

Two classes of cyclophosphazene monomers can be discerned. The first class of monomers makes use of an isolating spacer between the phosphazene ring and double bond. The second class consists of 1,1-disubstituted alkenes with the phosphazene directly bonded to the double bond [4,5]. So far only derivatives with fluorocyclotriphosphazene rings have been investigated (Figure 4.1). From the available NMR and polymerization data for both systems it can be concluded that the phosphazene ring influences the polymerization in two different ways. First, as the phosphazene ring is a strong electronegative group it can influence the electron distribution of the double bond, and thus the stability of a radical. Secondly, the inorganic substituent is a very spacious group and is therefore capable of shielding the polymer chain end from an incoming monomer. The use of a spacer group between the double bond and phosphazene ring is in this respect a very effective solution to circumvent problems arising from these influences. In this way the strong electronegative influence of the phosphazene ring is isolated from the double bond and also the steric hindrance at the polymerization site is reduced with this method.

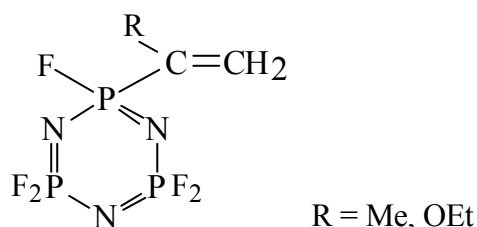


Figure 4.1 1,1-Alkenylfluorocyclotriphosphazenes

Another possibility is to counterbalance the electronegative effect from the phosphazene by an electropositive group situated at the same carbon atom of the alkene. NMR studies on 1,1-

alkenylfluorocyclotriphosphazenes revealed that the electron withdrawing effect of the phosphazene is indeed reduced when a second substituent with a large electron donating capacity is used [6]. However, these monomers could not be homopolymerized. This is probably a result of the large steric hindrance caused by the introduction of two substituents on the same carbon atom of the olefin. On the other hand radical copolymerization with a less steric demanding monomer (e.g. styrene) did result in copolymers and a wide range of phosphazene incorporation could be obtained. These observations clearly indicate that for 1,1-disubstituted monomers steric influence of the substituents govern whether or not addition takes place.

This Chapter discusses the reactivity of the monomers described in Chapter 2 in free-radical polymerization reactions. Based on the considerations above and the structure of the phosphazene derivatives it is expected that the styrene analogue, STP, behaves similar as styrene in radical reactions. The polymerization behavior of the novel 1,1-alkenylchlorocyclotriphosphazene precursors VAcP and PP is predicted to be significantly influenced by the steric hindrance at the reaction site.

## 4.3 Experimental

### Measurements

NMR spectra were recorded on a Varian Gemini-200 spectrometer operating at 199.98 ( $^1\text{H}$ ), 50.29 ( $^{13}\text{C}$ ) and 80.95 ( $^{31}\text{P}$ ) MHz.  $\text{CDCl}_3$  ( $^1\text{H}$  and  $^{13}\text{C}$ ) was used as internal standard.  $(\text{NPCl}_2)_3$  in  $\text{CDCl}_3$  was applied as external reference for  $^{31}\text{P}$  spectra. Gel permeation chromatography measurements were performed on a Spectra Physics AS 1000 system equipped with a Viscotek H502 viscometer and a Shodex RI-71 refractive index detector coupled to a Dawn (MALLS) light scattering apparatus.  $\text{CHCl}_3$  or THF were used as eluant. The columns were calibrated with polystyrene standards. Molecular weights were calculated using the universal calibration method ( $M_{w,v}$ ,  $M_{n,v}$ ), using the viscosity signal in combination with the concentration signal to calculate the intrinsic viscosity. The light scattering method combines the light scattering signal with the concentration signal to calculate the molecular weight of the fractions directly ( $M_{w,l}$ ,  $M_{n,l}$ ). Elemental analyses were carried out at the Microanalytical Department of the University of Groningen. Copolymer compositions were determined from weight percentage chlorine or  $^1\text{H}$  NMR spectra.

## Materials and procedures

All reactions were carried out in an atmosphere of dry oxygen-free nitrogen using standard Schlenck techniques. Methyl methacrylate (MMA, Janssen) and styrene (Janssen) were distilled from calcium hydride/copper bronze under reduced nitrogen atmosphere and stored at  $-20\text{ }^{\circ}\text{C}$ . 2,2'-Azobisisobutyronitrile (AIBN, Janssen) was recrystallized from methanol and stored under nitrogen at  $5\text{ }^{\circ}\text{C}$ . Toluene (Janssen) was distilled from sodium under nitrogen prior to use. All other reagents and solvents were used as received.

## Radical polymerization reactions

### Homopolymerization of STP

To a 23 wt% solution of STP in toluene was added 1 mol% AIBN. After three freeze-pump-thaw cycles the sample was placed in an oil bath at  $65 \pm 2\text{ }^{\circ}\text{C}$  for 48 h. The polymerization was terminated by precipitation in excess methanol. The polymer was collected by centrifugation, dissolved in methylene chloride and reprecipitated in methanol. The white powdery polymer was filtered, washed and vacuum dried. Yield 0.248 g (80%). Anal. Calc.: C, 29.37; H, 2.95; Cl, 34.68%. Found: C, 29.64; H, 3.01; Cl, 34.36%.  $^{31}\text{P}$  NMR  $\text{A}_2\text{B}$  type,  $\delta$  17.7 ( $\text{PCl}_2$ ), 36.5 ppm ( $\text{POrg}$ ),  $^2\text{J}_{\text{PP}}$  unresolved.

### Copolymerization of STP and MMA or styrene

The copolymerization reactions were conducted in a similar way as described above, however, using 50 wt% solutions in toluene. Composition and conversion data are summarized in Table 4.1.

### Attempted homopolymerization of VAcP

To 0.9 g (2.2 mmol) of VAcP was added 1 mol% AIBN. The sample was flushed 3 times with nitrogen and placed in an oil bath at  $50 \pm 2\text{ }^{\circ}\text{C}$  for 48 h. The  $^{31}\text{P}$  NMR spectrum of the resultant brown viscous oil showed no resonance signals of other ring products than VAcP.

### Copolymerization of VAcP and MMA

The copolymerization reactions were conducted in a similar way as described above. Composition and conversion data are summarized in Table 4.3.

### Copolymerization of VAcP with styrene

The following procedure was used for all copolymerization reactions. To a solution of 0.216 g (0.533 mmol) of VAcP in 1.1 ml (9.6 mmol) of styrene was added 16.6 mg (0.10

mmol, 1 mol%) of AIBN. After three freeze-pump-thaw cycles the sample was placed in an oil bath at  $50 \pm 2$  °C for 41 h. The reaction mixture was diluted with dichloromethane and precipitated in excess of methanol. The polymer was collected by centrifugation, dissolved in dichloromethane and reprecipitated twice in methanol. The white powdery polymer was filtered, washed and vacuum dried. Yield 0.53 g (43%). Found: Cl, 2.71%.  $^{31}\text{P}$  NMR A<sub>2</sub>B type,  $\delta$  17.4 (PCl<sub>2</sub>), 48.9 ppm (POrg),  $^2\text{J}_{\text{PP}}$  unresolved. Composition and conversion data are summarized in Tables 4.4 and 4.5.

#### Attempted homopolymerization of PP

To 0.198 g (0.549 mmol) of PP was added 1 mol% AIBN. The sample was flushed 3 times with nitrogen and placed in an oil bath at  $55 \pm 2$  °C for 2 days. After another 1 mol% AIBN was added, the solution was stirred for 20 hours more. The  $^{31}\text{P}$  NMR spectrum of the resultant brown viscous oil showed no resonance signals of other ring products than PP.

#### Copolymerization of PP with styrene

A typical procedure is as follows. To a solution of 0.298 g (0.826 mmol) of PP in 855  $\mu\text{l}$  (7.46 mmol) of styrene was added 1 mol% of AIBN. After three freeze-pump-thaw cycles, the sample was placed in an oil bath at  $55 \pm 2$  °C for 66 h. The reaction mixture was diluted with dichloromethane and precipitated in excess of methanol. The polymer was collected by centrifugation, dissolved in dichloromethane and reprecipitated in methanol. The white powdery polymer was filtered, washed and vacuum dried. Yield 0.59 g (55%). Found: Cl, 5.53%.  $^{31}\text{P}$  NMR A<sub>2</sub>B type,  $\delta$  16.4 (PCl<sub>2</sub>), 57.5 ppm (POrg),  $^2\text{J}_{\text{PP}}$  unresolved. Composition and conversion data are summarized in Table 4.7.

#### Copolymerization of PP and MMA

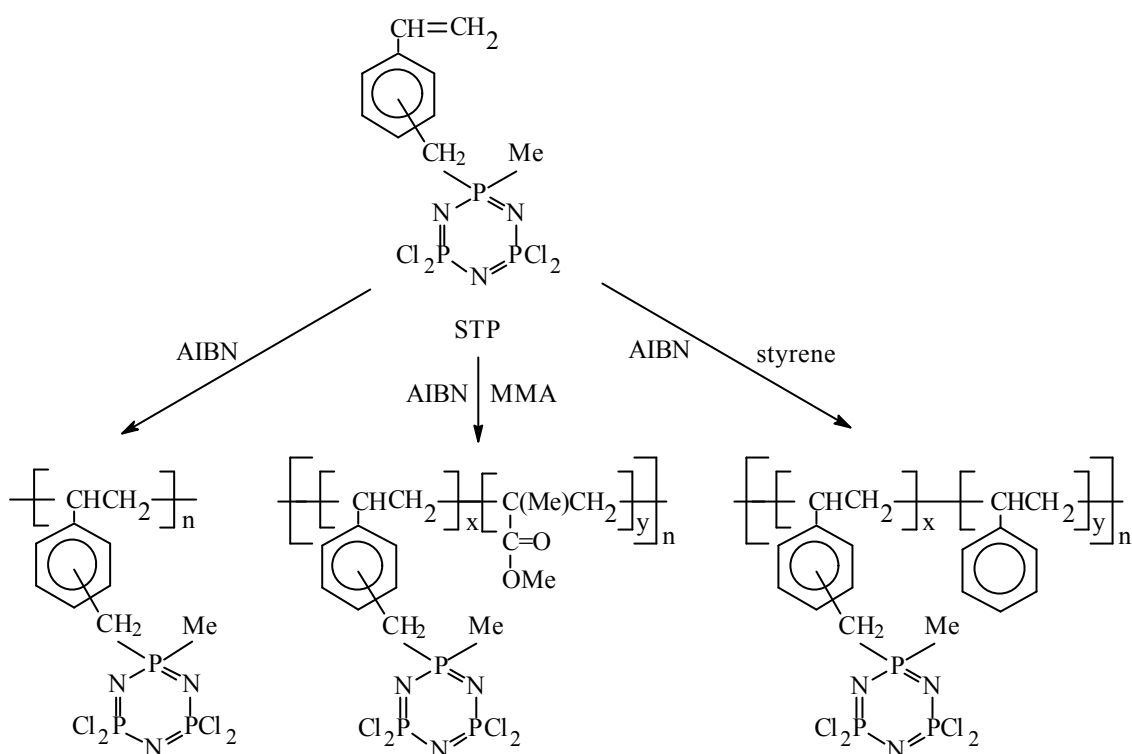
The copolymerization reactions were conducted in a similar way as described above. Composition and conversion data are summarized in Table 4.7.

## 4.4 Results and discussion

### 4.4.1 STP

The radical homo- and copolymerization reactions with STP shown in Scheme 4.1 proceed smoothly and yield polymers as white powders with moderate to high molecular

weights. The results of the (co)polymerizations of STP are summarized in Table 4.1. As can be seen the molecular weights determined from the light scattering method ( $M_{w,l}$ ,  $M_{n,l}$ ) are in good agreement with those obtained from the viscosimetric analysis ( $M_{w,v}$ ,



Scheme 4.1 Radical polymerization reactions of STP

Table 4.1 Composition, conversion and molecular weight data for (co)polymer from methyl(vinylbenzyl)phosphazene (STP) and MMA or styrene

| run no.        | mol% STP feed | mol% STP polymer | time (min)       | conversion (%) | $\bar{M}_{w,l}$ ( $\times 10^{-3}$ ) | $\bar{M}_{n,l}$ ( $\times 10^{-3}$ ) | $\bar{M}_{w,v}$ ( $\times 10^{-3}$ ) | $\bar{M}_{n,v}$ ( $\times 10^{-3}$ ) |
|----------------|---------------|------------------|------------------|----------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 1              | 5.0           | 9.0              | 13               | 8              | 180                                  | 100                                  | 200                                  | 95                                   |
| 2              | 10.0          | 16.5             | 15               | 5              | 220                                  | 160                                  | 260                                  | 120                                  |
| 3 <sup>a</sup> | 17.7          | 24.3             | 16               | 5              | -                                    | -                                    | 160                                  | 20                                   |
| 4 <sup>a</sup> | 36.3          | 38.6             | 40               | 11             | -                                    | -                                    | 10                                   | 5                                    |
| 5 <sup>a</sup> | 59.9          | 48.8             | 60               | 9              | -                                    | -                                    | 40                                   | 5                                    |
| 6              | 100           | 100              | 48 <sup>b</sup>  | 80             | 65                                   | 35                                   | 80                                   | 40                                   |
| 7 <sup>c</sup> | 9.5           | 10*              | 45               | 2              | -                                    | -                                    | 50                                   | 30                                   |
| 8 <sup>c</sup> | 33.7          | 34*              | 3.5 <sup>b</sup> | 19             | -                                    | -                                    | 85                                   | 50                                   |

<sup>a</sup> Waters ALC/GPC 150C; <sup>b</sup> hours; <sup>c</sup> styrene as comonomer; \* <sup>1</sup>H-NMR



$M_{n,v}$ ). All the inorganic-organic copolymers are soluble in common organic solvents as toluene, chloroform and dichloromethane. Only THF appears to be a poor solvent because STP/MMA-copolymer samples with phosphazene contents of 38.6 mol% and higher could not be dissolved completely.

Furthermore, as shown in Table 4.1, the molecular weight of these samples are one order of magnitude smaller than is observed for the samples 1-3. This phenomenon has been observed for other radical copolymerizations involving vinylphosphazenes and organic monomers, and has been attributed to the phosphazene monomer acting as a chain transfer or terminating agent [4,5,7,8]. However, the same behavior is observed for the radical copolymerization of styrene with MMA, where with increasing contents of styrene in the feed the molecular weights of the resulting copolymers also decrease [9]. This phenomenon is merely the result of a shift to smaller  $k_p/k_t$  ratios for the radical polymerization reaction. Styrene has a smaller rate constant of propagation ( $k_p = 116 \text{ l mol}^{-1} \text{ s}^{-1}$ ) and a higher rate constant of termination ( $k_t = 108 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ ) compared with MMA ( $k_p = 381 \text{ l mol}^{-1} \text{ s}^{-1}$  and  $k_t = 35 \times 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ ) [10]. And thus with higher styrene feed ratios the overall rate of monomer consumption of the copolymerization reaction will be lowered and also the molecular weight of the polymer. Considering STP as a styrene derivative and keeping in mind that there are no indications that the phosphazene ring participates in any transfer or termination reaction, the observed lowering of the molecular weight can be assigned to the same effect as in the system of styrene/MMA.

To investigate the composition of the copolymers the copolymerization reactivity ratios for the polymerization system with STP and MMA were calculated. Once these ratios are determined one can calculate the copolymer composition over the entire range of the monomer feed even when the initial monomer feed changes during the polymerization reaction. In the case of a copolymerization with two monomers, where only the terminal unit of the polymer chain influences the rate constant for propagation, the composition of the copolymer formed at the initial stage of the polymerization is given by the well-known copolymer composition equation of Mayo and Lewis [11]:

$$\frac{m_1}{m_2} = \frac{M_1}{M_2} \frac{r_1 M_1 + M_2}{r_2 M_2 + M_1}$$

with  $m_1$  = mole fraction of monomer 1 in the copolymer,  $M_1$  = mole fraction of monomer 1 in the feed and where the reactivity ratios  $r_1$  and  $r_2$  are defined as:

$$r_1 = k_{11}/k_{12} \quad \text{and} \quad r_2 = k_{22}/k_{21}$$

The subscripts 1 and 2 refer to the monomers STP and MMA, respectively. The first number of the propagation constant identifies the terminal radical monomer unit of the growing polymer chain, while the second denotes the adding monomer. For instance,  $k_{12}$  means the rate of addition of a MMA monomer to a STP radical chain end.

In order to calculate the reactivity ratios the above equation is transformed into a linearized form. The most frequently used linearization methods are developed by Fineman and Ross and by Kelen and Tüdös [12,13]. The method derived by Kelen and Tüdös is however preferred over the FR-method as it gives more accurate values for the reactivity ratios. The linear KT-equation is given by:

$$\eta = \left( r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha}$$

where

$$\eta = G/(\alpha + F) \quad \text{and} \quad \xi = F/(\alpha + F)$$

and

$$\alpha = \sqrt{F \min F \max}$$

with

$$G = M(m - 1)/m \quad \text{and} \quad F = M^2/m.$$

Here  $M$  and  $m$  are mole ratios of the monomers in the feed and the copolymer, respectively. The arbitrary constant  $\alpha$  is used for minimizing experimental errors by distributing the experimental data uniformly along the interval (0, 1). As already mentioned before, these equations are only valid as long as the monomer feed ratio is not changed. In general, the error caused by the change in monomer feed ratio during polymerization is considered sufficiently small when conversions up to 10 wt% are used for the calculation. To satisfy this condition the copolymerizations of run no. 1-5 were not allowed to exceed this limit.

With the composition data in Table 4.1 and the linearized equation by Kelen-Tüdös the  $\eta$ - $\xi$  plot in Fig. 4.2 was calculated. As a straight line satisfactory appears to fit the data (correlation coefficient equal to 0.998) one can conclude that the terminal model is valid and that no penultimate effect is operative for this copolymerization system [13]. The calculated values for  $r_1$  (= 0.21) and  $r_2$  (= 0.48) are given in Table 4.2. Calculation of reactivity ratios using a non-linear minimization technique combined with a error-in-variables method [14]

yielded values of  $r_1, r_2 = 0.17, 0.47$  [15] which are in close

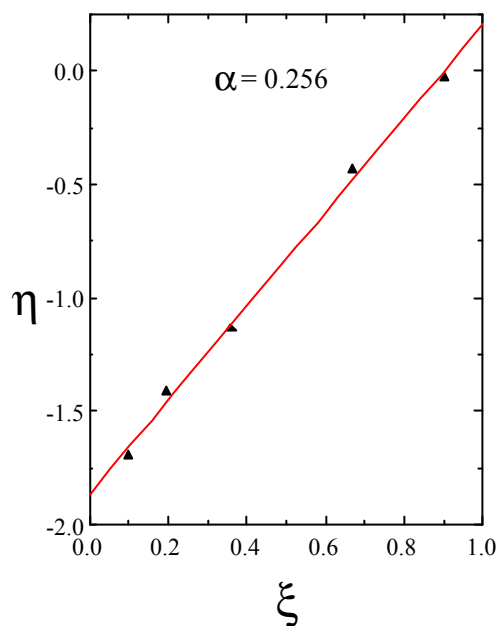


Figure 4.2 Kelen-Tüdös plot for the copolymerization of STP with MMA

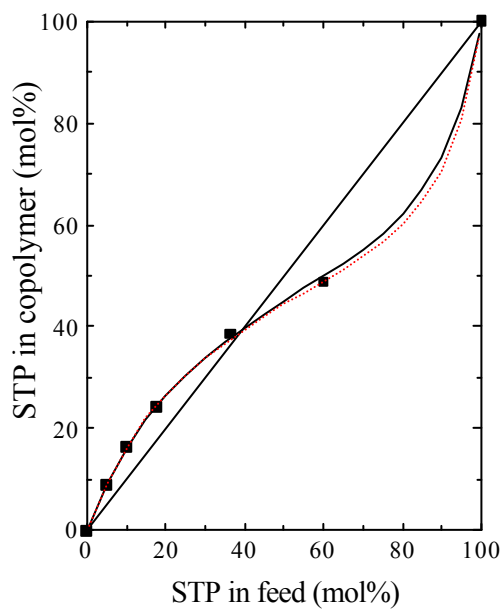


Figure 4.3 Copolymer composition curves for the radical copolymerization of STP with MMA (— calculated for  $r_1 = 0.21$ ,  $r_2 = 0.48$  and --- with  $r_1 = 0.17$ ,  $r_2 = 0.47$ )

agreement with those calculated by the Kelen-Tüdös method. With these two sets of reactivity ratios the copolymer composition curves, as shown in Figure 4.3, were calculated according to the copolymer composition equation of Mayo and Lewis. It can be seen that the experimental data are fitted very well by the two curves, whereas difference between the two curves is negligible.

The reactivity ratio  $r_1$  for STP (0.21) is slightly smaller compared with that of styrene (0.52). As electronic effects are excluded, this decrease is probably caused by the steric demanding phosphazene substituent which renders the double bond less accessible for the addition of another phosphazene monomer. From the two copolymerizations which were carried out with styrene (run no. 7 and 8) it follows that the ratio of STP to styrene in the monomer feed is retained in the composition of the obtained copolymers. This confirms that the phosphazene containing monomer has a reactivity which is comparable with that of styrene.

Table 4.2 Reactivity ratios

| M <sub>1</sub>       | M <sub>2</sub> | r <sub>1</sub> | r <sub>2</sub> |
|----------------------|----------------|----------------|----------------|
| STP                  | MMA            | 0.21           | 0.48           |
| Styrene <sup>a</sup> | MMA            | 0.52           | 0.46           |

<sup>a</sup> From Ref. 16

Because both  $r_1$  and  $r_2$  are smaller than unity and the value of  $r_1r_2$  is close to zero, the monomers prefer to cross-propagate resulting in an alternating-like copolymer. This tendency for alternation is mainly a result of the electronic interaction between the growing chain end and monomer. The existence of such an interaction can be shown by comparing the nature of the substituents attached to the vinyl groups of the monomers. In the case of MMA one deals with an electron acceptor [ $\delta^{13}\text{C}(=\text{CH}_2) = 124.7$  ppm], whereas in styrene the substituent can be regarded as an electron donor [ $\delta^{13}\text{C}(=\text{CH}_2) = 113.7$  ppm]. Considering now a growing chain end with an electron donor (or acceptor) substituent X and a monomer with an electron acceptor (or donor) Y, which differ sufficiently in polarity, then the partial bond that forms between them in the transition state is stabilized by the induced polarity. This lowers the energy of the transition state and consequently the activation energy. For the addition step with equal substituents this stabilizing effect is absent resulting in a higher activation energy than in the former case [16]. However, for the copolymerization of STP with MMA there is also a contribution which is steric in nature, and amplifies the cross-propagation.

In summary, we can say that the polymerization behavior of the new styrene substituted chlorocyclotriphosphazene resembles that of styrene. The  $\text{PCl}_2$  groups in the polymers prepared are susceptible to hydrolysis. The same behavior is observed for the phosphazene monomer as it becomes gradually yellow, when standing in open contact with air. The hydrolytic stability can be improved by substitution of the remaining  $\text{PCl}_2$  groups.

#### 4.4.2 VAcP

A comparison of the  $^{13}\text{C}$  NMR spectra of vinyl acetate and VAcP shows the strong electron withdrawing character of the phosphazene ring. For vinyl acetate the  $\beta$ -carbon of the vinyl group has a resonance signal at 96.8 ppm, while for VAcP the signal is shifted downfield to 119.2 ppm. For the  $\alpha$ -carbon of the vinyl group also a downfield shift is observed from 141.8 for vinyl acetate to 148.2 ppm for the inorganic monomer. Despite the fact that the carbon atoms of the double bond have become more electron-deficient in comparison with vinyl acetate, the  $\delta$   $^{13}\text{C}(=\text{CH}_2)$  value of 119.2 ppm is intermediate between that of MMA (124.7 ppm) and styrene (113.7 ppm). As these monomers can be homopolymerized easily under radical conditions, it seems reasonable to assume that the inorganic precursor is also suitable for radical polymerization reactions. However, the presence of the steric demanding phosphazene and acetoxy group directly bonded to the same carbon atom of the olefin will undoubtedly hinder the polymerization reaction to a large extent. As an example, this phenomenon is observed when the  $\alpha$ -hydrogen atom of the styrene double bond is replaced by a larger substituent, e.g. a methyl group in the case of  $\alpha$ -methylstyrene. Although styrene homopolymerizes smoothly under normal radical conditions used, the  $\alpha$ -methylstyrene does not, because the increased steric hindrance at the double bond results in an exceptional low ceiling temperature [17]. Thus based on these structural and electronic considerations, the vinyl acetate derivative is expected not to undergo radical homopolymerization, but can be involved in radical copolymerization.

##### 4.4.2.1 Copolymerization reactions of VAcP and MMA

The results of the (co)polymerization reactions of VAcP are summarized in Tables 4.3-4.5. As expected VAcP could not be homopolymerized under the conditions used, but bulk copolymerizations with MMA and styrene did produce polymers.

When MMA was used as comonomer only very small amounts of VAcP were incorporated (see Table 4.3). Because VAcP appears to have a very low reactivity in the radical copolymerization reaction with MMA, this system was not investigated further.

However, from the VAcP/MMA copolymerization data in Table 4.3 several conclusions can be drawn. The small amounts of VAcP incorporated show that addition of a MMA monomer to a MMA polymer chain end is largely preferred. As with very high feed ratios of VAcP the incorporation of cyclophosphazene is still very small, the rate of addition of a phosphazene monomer to a MMA polymer chain end must be small as well. Furthermore, the observed decrease in molecular weight with higher feed ratios of VAcP suggests that once a phosphazene polymer chain end is formed addition of another monomer is greatly hindered. Because the vinyl acetate derivative is unable to homopolymerize and a very low incorporation of VAcP in the MMA copolymers is found, it is obvious that addition of VAcP monomer to a VAcP radical chain end does not take place. From the reasoning given above it is clear that these polymerizations are governed by steric hindrance already present at the polymerization site and size of the approaching monomer.

Table 4.3 Composition, conversion and molecular weight data for copolymers derived from VAcP and MMA

| run no.          | mol% VAcP feed | mol% VAcP polymer | time (h) | conversion (%) | $\bar{M}_{w,1}$ ( $\times 10^{-3}$ ) | $\bar{M}_{n,1}$ ( $\times 10^{-3}$ ) | $\bar{M}_{w,y}$ ( $\times 10^{-3}$ ) | $\bar{M}_{n,y}$ ( $\times 10^{-3}$ ) |
|------------------|----------------|-------------------|----------|----------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 1 <sup>a,b</sup> | 5.4            | 0.3#              | 24       | 35             | 240                                  | 45                                   | 220                                  | 60                                   |
| 2 <sup>c</sup>   | 15.0           | 1.2#              | 20       | 39             | 125                                  | 70                                   | 105                                  | 50                                   |
| 3 <sup>c</sup>   | 29.6           | 1.3#              | 18       | 20             | 80                                   | 50                                   | 65                                   | 35                                   |

<sup>a</sup> GPC measurement with CHCl<sub>3</sub> as eluant; <sup>b</sup> bimodale molecular weight distribution;

<sup>c</sup> GPC measurement with THF as eluant

# el. analyses

#### 4.4.2.2 Low conversion copolymerizations of VAcP and styrene

When the less steric hindered styrene is used as comonomer, bulk copolymerization with VAcP affords copolymers with reasonable amounts of VAcP incorporated (see Table 4.4). With feed ratios of 40 mol% and higher of phosphazene monomer no polymer could be recovered.

To determine the monomer reactivity ratios by the Kelen-Tüdös method the polymerizations were terminated at conversions below 10 wt% [13]. As can be seen in Figure 4.4 the calculated  $\eta$ - $\xi$  plot does not represent a straight line. This implicates that the VAcP/styrene radical copolymerization reaction is not described adequately by the terminal model. Also from literature examples are known, viz. 1,1-alkenylfluorocyclophosphazenes with

styrene, where the radical copolymerization



Table 4.4. Composition and conversion data for copolymers derived from VAcP and styrene at low conversion

| run no. | mol% VAcP feed | mol% VAcP polymer | time (h) | conversion (%) |
|---------|----------------|-------------------|----------|----------------|
| 4       | 2.5            | 2.4               | 1.5      | 2.5            |
| 5       | 4.7            | 4.5               | 2        | 3.1            |
| 6       | 9.9            | 6.0               | 2.5      | 3.2            |
| 7       | 15.2           | 7.0               | 4        | 4.5            |
| 8       | 20.0           | 10.0              | 7.5      | 4.9            |
| 9       | 25.0           | 11.8              | 8        | 6.9            |
| 10      | 32.8           | 12.2              | 16.5     | 6.7            |
| 11      | 40.0           | 0                 | 50       | 0              |

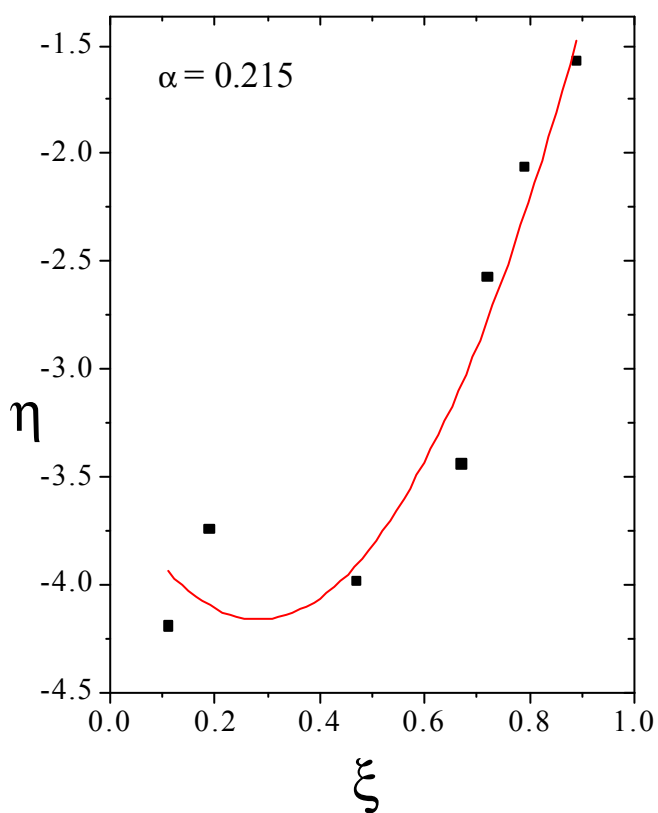


Figure 4.4  $\eta$ - $\xi$  Plot for the low conversion polymerization of VAcP and styrene

behavior has to be described by the penultimate model rather than by the terminal model [1,2].

Calculation of reactivity ratios for the penultimate model using a non-linear minimization technique and the error-in-variables method led not to convergence [14,15]. The reason for this is not clear, but one has to keep in mind that the error in determining the composition and conversion is relative large at low conversions. Another explanation could be that the phosphazene precursor has a low solubility in styrene and that at high feed ratios VAcP is not completely dissolved on a microscale although the solutions looked clear. These errors are inherent to the system and the only possibility left to calculate the reactivity ratios for this system is to find a method which is less sensitive for errors in the data.

Therefore use was made of a new iterative linear least-squares method developed by Mao and Huglin [18,19]. Their method can be applied for the calculation of reactivity ratios both for the terminal model, as for the penultimate model with  $r_2 = 0$ , using copolymerization data obtained at high conversions ( $> 10$  wt%).

#### 4.4.2.3 High conversion copolymerizations of VAcP and styrene

To obtain a maximum yield of polymer copolymerizations were carried out for 40-45 hours. The results are summarized in Table 4.5 and Figures 4.5 and 4.6.

A maximum incorporation of 20.2 mol% of VAcP was achieved with a feed ratio of 35 mol% of VAcP in the feed. As the molecular weights of the resulting polymers showed a unimodale distribution it can be assumed that no thermal polymerization has occurred. From Table 4.5 it can be seen that the molecular weights calculated from the light scattering data ( $\overline{M}_{w,l}$ ,  $\overline{M}_{n,l}$ ) are in good agreement with those obtained from the viscosimetric analysis ( $\overline{M}_{w,v}$ ,  $\overline{M}_{n,v}$ ). As observed for the copolymerization of VAcP with MMA, the molecular weight and conversion decrease rapidly with increasing phosphazene content in the feed. This phenomenon, which is found for most copolymerizations with phosphazene derivatives as comonomers, has been ascribed to the phosphazene compound giving rise to an increased chance on termination (increase in  $k_t$ ) or transfer reactions [4,5]. However, in this context another point should be considered, because this phenomenon can also be related to a decrease in the rate of propagation ( $k_p$ ) for the polymerization reaction. The large substituents on the double bond of VAcP can hinder the addition of another monomer. This will retard the polymerization reaction (lowering of  $k_p$ ) and subsequently the obtained molecular weights and conversions will be lower. This effect has been shown to be operative for  $\alpha$ -(substituted methyl)acrylates. Here the steric hindrance caused by the substituents results in a smaller rate of propagation

(k<sub>p</sub>) and

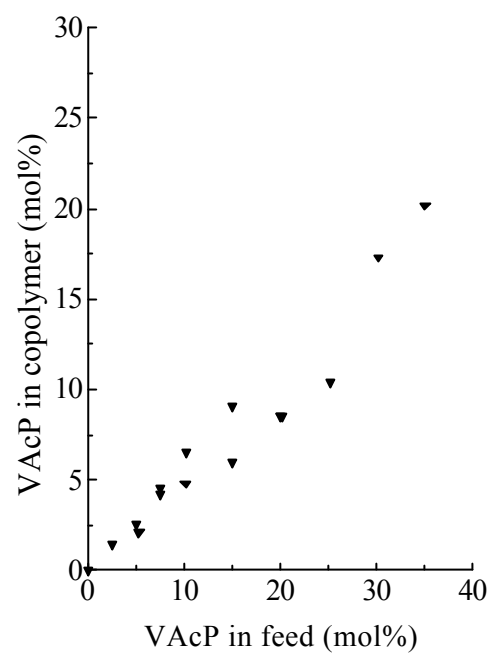


Figure 4.5 Feed-incorporation plot for high conversion polymerization of VAcP and styrene

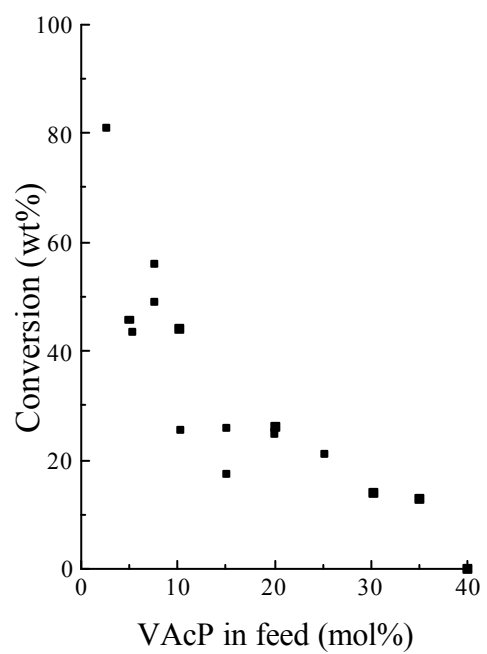


Figure 4.6 Feed-conversion plot for high conversion polymerization of VAcP and styrene

Table 4.5 Composition, conversion and molecular weight data for copolymers derived from VAcP and styrene at high conversion

| run no.         | mol% VAcP feed | mol% VAcP polymer | time (h) | conversion (%) | $\bar{M}_{w,1}$ ( $\times 10^{-3}$ ) | $\bar{M}_{n,1}$ ( $\times 10^{-3}$ ) | $\bar{M}_{w,y}$ ( $\times 10^{-3}$ ) | $\bar{M}_{n,y}$ ( $\times 10^{-3}$ ) |
|-----------------|----------------|-------------------|----------|----------------|--------------------------------------|--------------------------------------|--------------------------------------|--------------------------------------|
| 12 <sup>a</sup> | 2.5            | 1.4*              | 40       | 81.0           | 165                                  | 70                                   | 155                                  | 50                                   |
| 13 <sup>a</sup> | 5.0            | 2.5#              | 45       | 45.7           | 140                                  | 95                                   | 135                                  | 85                                   |
| 14 <sup>b</sup> | 5.3            | 2.1#              | 40       | 43.5           | 125                                  | 75                                   | 125                                  | 65                                   |
| 15 <sup>a</sup> | 7.5            | 4.5#              | 45       | 56.0           | 100                                  | 65                                   | 100                                  | 40                                   |
| 16              | 7.5            | 4.2#              | 40       | 49.0           | -                                    | -                                    | -                                    | -                                    |
| 17 <sup>a</sup> | 10.1           | 4.8#              | 40       | 44.1           | 95                                   | 65                                   | 95                                   | 55                                   |
| 18 <sup>a</sup> | 10.2           | 6.5#              | 45       | 25.5           | 120                                  | 70                                   | 110                                  | 60                                   |
| 19 <sup>a</sup> | 15.0           | 6.0#              | 45       | 25.9           | 90                                   | 65                                   | 90                                   | 55                                   |
| 20              | 15.0           | 9.1*              | 40       | 17.5           | -                                    | -                                    | -                                    | -                                    |
| 21 <sup>a</sup> | 20.0           | 8.5*              | 40       | 25.0           | 75                                   | 50                                   | 75                                   | 35                                   |
| 22 <sup>a</sup> | 20.1           | 8.5#              | 40       | 26.1           | 70                                   | 50                                   | 70                                   | 45                                   |
| 23 <sup>a</sup> | 25.1           | 10.4#             | 40       | 21.2           | 60                                   | 45                                   | 65                                   | 45                                   |
| 24 <sup>a</sup> | 30.2           | 17.3#             | 70       | 13.9           | 60                                   | 25                                   | 55                                   | 25                                   |
| 25              | 35.0           | 20.2*             | 40       | 12.8           | -                                    | -                                    | -                                    | -                                    |

<sup>a</sup> GPC measurement with THF as eluant; <sup>b</sup> GPC measurement with CHCl<sub>3</sub> as eluant

\* <sup>1</sup>H-NMR, # el. analyses

even a considerably smaller rate of termination ( $k_t$ ) than those for MMA [20-22]. From the small reactivity ratio values reported in literature for cyclophosphazene monomers it can be concluded that in copolymerization reactions these monomers also give rise to a lowering of the propagation rate [1,2,4,5]. Moreover, for an increased chance on termination or transfer reactions no supporting evidence is given. Therefore the decrease in molecular weight and conversion is most likely due to the lowering of the  $k_p$  instead of an increase in  $k_t$ .

With our experimental data from Table 4.5 convergence was reached when calculation was carried out for the terminal model. From the  $\eta$ - $\xi$  plot at the last iteration shown in Figure 4.7 it can be seen that there is some scattering in the data (the linear fit has a correlation coefficient equal to 0.89012). This is also reflected in the large 95% joint confidence region for this system (Figure 4.8, system 1). The calculated values for  $r_1$  and  $r_2$  are summarized in Table 4.6.

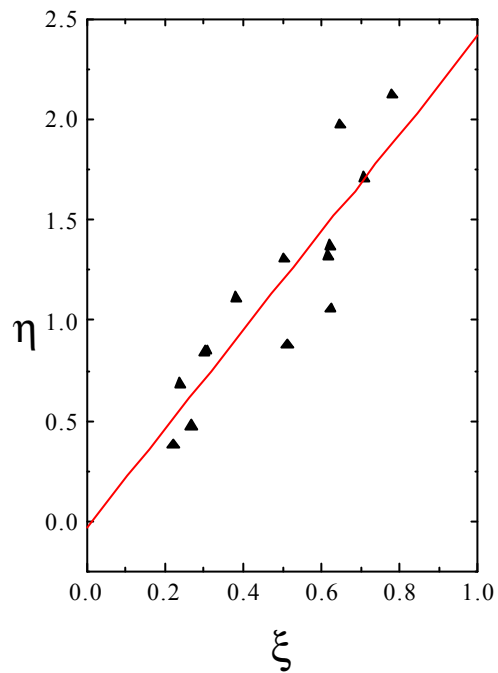


Figure 4.7  $\eta$ - $\xi$  Plot at the last iteration for the experimental data from the high conversion polymerization of VAcP and styrene (system 1)

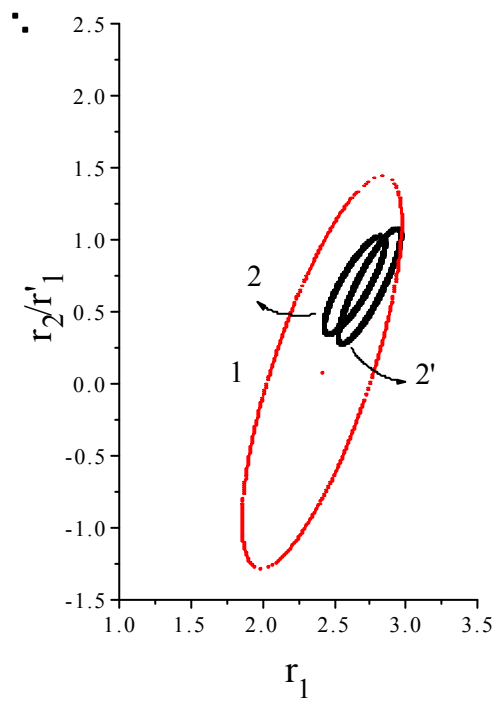


Figure 4.8 95% JCR plots from the different methods (see text)

Table 4.6 Calculated reactivity ratios for the high conversion polymerization of VAcP and styrene

| System          | Model   | $r_1$         | $r'_1$        | $r_2$         | $r'_2$ |
|-----------------|---------|---------------|---------------|---------------|--------|
| 1               | exp/ter | $2.4 \pm 0.4$ | -             | $0.1 \pm 1.1$ | -      |
| 2               | lin/ter | $2.6 \pm 0.2$ | -             | $0.7 \pm 0.3$ | -      |
| 2' <sup>a</sup> | lin/pen | $2.7 \pm 0.2$ | $0.7 \pm 0.1$ | 0             | 0      |

$M_1 = \text{styrene}$ ; <sup>a</sup> for penultimate model with  $r_1 = k_{111}/k_{112}$ ,  $r'_1 = k_{211}/k_{212}$ ,  $r_2 = k_{222}/k_{221}$  and  $r'_2 = k_{122}/k_{121}$

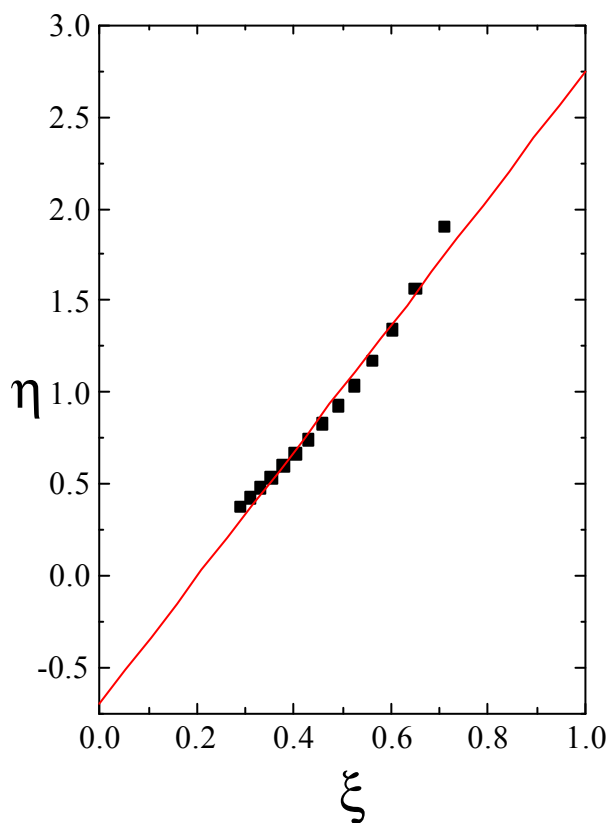


Figure 4.9  $\eta$ - $\xi$  Plot at the last iteration for system 2' (correlation coefficient 0.98998)

When using the experimental data for the penultimate model with  $r_2 = 0$ , calculations led not to convergence. Therefore the feed-incorporation data were fitted with a linear function (Figure 4.5) while the feed-conversion data (Figure 4.6) were fitted with an exponential

function. From these functions new data sets were calculated which were used for further calculations. The monomer reactivity ratios were calculated for both the terminal model (system 2) and penultimate model with  $r_2 = 0$  (system 2'). The results are given in Table 4.6. The use of a polynomial function for fitting the feed-incorporation data gave similar values for the reactivity ratios.

From the  $\eta$ - $\xi$  plots at the last iteration of the calculations for the 2 different systems (in Figure 4.9 only system 2' is given) it can be seen that with these simulated data a nearly linear result is obtained. As a result the corresponding 95% joint confidence intervals are also considerably smaller (see Figure 4.8).

A comparison of the results obtained with the experimental and fitted data for the terminal model reveals that the value of  $r_2$  ( $0.1 \pm 1.1$  and  $0.7 \pm 0.3$ ) are small but higher than zero. The value of  $r_1$  ( $2.4 \pm 0.4$  and  $2.6 \pm 0.2$ ) seems to be not large enough to account for the observed polymerization behavior. From the low value (20.2 mol%) of maximum incorporation and the observation that with feed contents of 40 mol% and higher of VAcP no polymerization takes place, it seems that the penultimate model with  $r_2 = 0$  will be a better solution for this system. When we consider the results for the penultimate model, the values of  $r_1$  and  $r'_1$  (Table II, system 2') are more in line with what is expected. However, these values are the result of assumptions and should be considered only as an indication.

#### 4.4.3 PP

The results of the free radical polymerization reactions with the propene derivative PP are listed in Table 4.7. Homopolymerization of PP failed, whereas in a copolymerization reaction with MMA only a very small amount of the inorganic component was incorporated, just as was observed for the other 1,1-disubstituted inorganic monomer VAcP. In the literature the polymerization behavior of similar compounds, the 1,1-alkenylfluorocyclotriphosphazenes  $N_3P_3F_5C(Me)=CH_2$  and  $N_3P_3F_5C(OEt)=CH_2$ , has been described [1,2,4,5]. These precursors are also unable to undergo homopolymerization. However, in copolymerization with the less steric hindered monomer styrene, copolymers are obtained which contain large amounts of the inorganic monomer. Thus the reluctance of the 1,1-disubstituted inorganic monomers to undergo radical homo- and copolymerization reactions with MMA is very probably due to steric hindrance at the reaction site.

In the copolymerization reaction of PP with styrene 18 mol% of PP is incorporated at a conversion of only 1.4 wt% with 61 mol% of PP in the feed. Compared with the system  $N_3P_3F_5C(Me)=CH_2$ /styrene it is noted that with the fluoro derivative a maximum incorporation



of 37 mol% (with 80 mol% in the feed) can be achieved at a conversion of 37 wt% [4]. As the polarization of the double bond is almost the same for both PP and the fluoro derivative (see Table 2.1) the difference in polymerization behavior between the latter two inorganic monomers must be due to a larger steric hindrance in the case of PP. This clearly shows that the substituent, e.g. the iso-propyl group, on the same phosphorus atom as the double bond exerts a large influence on the polymerization behavior of monomers like PP and VAcP.

Table 4.7 Composition, conversion and molecular weight data for copolymers from PP

| run <sup>a</sup><br>no. | mol% PP |         | time<br>(days) | conversion<br>(%) | $\bar{M}_{w,l}$<br>( $\times 10^{-3}$ ) | $\bar{M}_{n,l}$<br>( $\times 10^{-3}$ ) | $\bar{M}_{w,v}$<br>( $\times 10^{-3}$ ) | $\bar{M}_{n,v}$<br>( $\times 10^{-3}$ ) |
|-------------------------|---------|---------|----------------|-------------------|---|---|---|---|
|                         | feed    | polymer |                |                   |   |   |   |   |
| 1                       | 10      | 4.5     | 3              | 55                | 70                                      | 35                                      | 65                                      | 40                                      |
| 2 <sup>b</sup>          | 40      | 13.5    | 5              | 17                | 55                                      | 20                                      | 55                                      | 25                                      |
| 3                       | 61      | 18      | 3              | 1.4               | 15                                      | 10                                      | 15                                      | 10                                      |
| 4 <sup>b</sup>          | 5       | 0.3     | 3 (h)          | 67                | 730                                     | 370                                     | 540                                     | 100                                     |

<sup>a</sup> Run no. 1-3 with styrene and no. 4 with MMA as comonomer; <sup>b</sup> bimodale molecular weight distribution

The behavior of PP in copolymerization reactions with styrene resembles closely that of VAcP. Both conversion and molecular weight exhibit a distinct decrease with increasing amounts of PP in the feed. Moreover, the molecular weights are of the same order as observed for the VAcP/styrene copolymers. Although the maximum obtainable incorporation of both PP and VAcP is about 20 mol%, the required amount of inorganic monomer in the feed is larger for PP (Table 4.5). The PP/styrene system was not investigated further, because it offers no additional advantages over the VAcP/styrene system. Although the reactivity ratios were not calculated one can draw some conclusions by comparing the systems discussed above. For instance, the addition of a VAcP monomer to a styrene chain end is preferred over that of PP. The reason for this is probably electronic in nature as for both inorganic monomers the steric hindrance will be roughly the same at the reaction site in this propagation step. Considering the substituents on the same carbon atom of the double bond it is noted that for VAcP electron withdrawing (captive) and donating (dative) groups are present, being the phosphazene ring and acetoxy group, respectively. For PP only an electron withdrawing phosphazene ring is present as the methyl group has neither electron donating nor withdrawing capabilities. It is known that radicals formed from capto-dative (cd) monomers can be more stable than those formed from

double bonds bearing only a captive or dative substituent [23,24]. Thus reaction of VAcP with a styrene radical results in a more stabilized radical chain end making this propagation step energetically more favourable than the reaction where PP adds to a styrene radical chain end.

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