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Synthesis of a perfluorinated azo initiator

Application to the determination of the recombination/disproportionation rate during the polymerization of styrene

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Summary: A method to determine the recombination/disproportionation rate during the polymerization of styrene is described. In this method, a perfluorinated azo initiator used to prepare a perfluorinated polystyrene was first synthesized. Then, the recombination/disproportionation rate was calculated by comparing the number-average molecular weight ($\overline{DP}_n$) and the fluorine content in weight of this resulting polystyrene.

Introduction

In free-radical polymerization, the mode of bimolecular termination is very important: this affects the degree of polymerization and the molecular weight distribution of the resulting polymer. Concerning the synthesis of telechelic oligomers, this controls whether the oligomer will be telechelic or not.

Many techniques were used to estimate recombination/disproportionation rate in the polymerization of styrene. The oldest and the most employed ones are tracer techniques (1-3) using for example ^{14}C AIBN as the labeled probe. Mayo and Matheson (4) acceded to the ratio by comparing the molecular weights and the rates of initiation. Bamford (5,6) used the coupling technique which directely involved initiator fragments. Baker (7) proposed a correlation between molecular weight distribution and the percentage of combination. Bamford (8,9) described a kinetic technique based on grafting and gelation, for the determination of the nature of termination reaction quantitatively. Two others methods can be cited: bifunctional initiation (10) and model compounds (11). All these researchers appear to agree that termination of polystyrene takes place almost exclusively by combination, over a wide range of temperatures (12). Meanwhile, some authors such as Olaj (13,16) and Berger (14,15) maintain that disproportionation in styrene polymerization has been underestimated, since it was found a percentage of combination of 85 to 60 % between 30 and 40°C. Labeled tracer technique is the most practicable and accurate method but it is also the most delicate. This requires cautions in the isolation of the polymer, particularly low-molecular-weight material which contains a relatively large proportion of end-group labeled with radio-tracer.

To avoid these drawbacks, it was interesting to synthesize a polymer from perfluorinated azo compound (17); The fluorine content in this polymer can be very high

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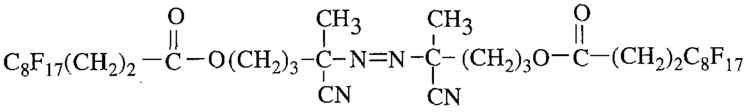
and then easily titrated according to the high weight of these perfluorinated groups. In order to get an adequate tracer, it has been chosen with a sufficient weight such as perfluorooctyl radical: C_8F_{17}. Accordingly the fluorinated azo diester 1, used as initiator in the polymerization of styrene was synthesized. By measuring the number-average molecular weight ($\overline{DP}_n$) and the fluorine content in weight of the resulting polystyrene, the members of initiators fragments incorporated in one polymer molecule can be determined.



$$C_8F_{17}(CH_2)_2-\overset{O}{\overset{\|}{C}}-O(CH_2)_3-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-(CH_2)_3O-\overset{O}{\overset{\|}{C}}-(CH_2)_2C_8F_{17}$$

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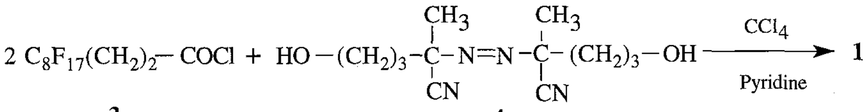
Results and discussion

Azo diester 1 is obtained by condensation of perfluorinated acid chloride 3 with azo diol 4 (4,4'-azobis-(4-cyanopentanol) or ACP. This perfluorinated acid chloride 3 is prepared by reaction of 3-perfluorooctylpropionic acid 2 with an excess of thionyle chloride.The reaction is controled by IR analysis by evolution of COCl peak at 1800 cm^{-1}. Reaction of acid chloride 3 with azo diol 4 yields the fluorinated diester 1 with 70% yield. It is characterized by IR analysis with the (C=O) peak at 1738 cm^{-1}. On ^1H NMR spectrum a triplet is observed, due to CH_2 in α position to the oxygen atom at 4,25 ppm.

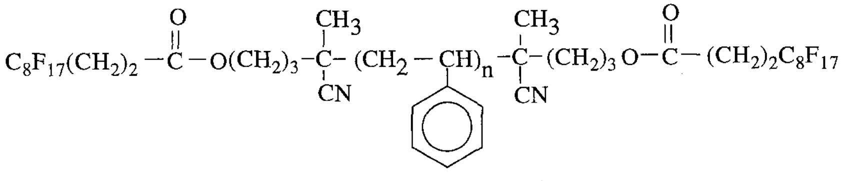
$$\underset{2}{C_8F_{17}(CH_2)_2-CO_2H} + SOCl_2 \longrightarrow \underset{3}{C_8F_{17}(CH_2)_2-COCl}$$



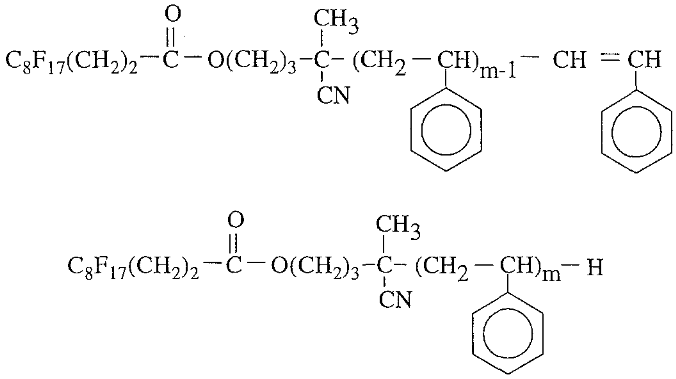
$$2\ C_8F_{17}(CH_2)_2-COCl + HO-(CH_2)_3-\underset{CN}{\overset{CH_3}{C}}-N=N-\underset{CN}{\overset{CH_3}{C}}-(CH_2)_3-OH \xrightarrow[\text{Pyridine}]{CCl_4} 1$$

3 4

It is known that radical polymerizations are terminated by recombination and/or disproportionation reactions (18). Under these conditions styrene polymerizations initiated by azo compound 1 may lead to these structures:



(termination by recombination)



(termination by disproportionation)

The optimum recombination/disproportionation percentage depends upon the choice of polystyrene $\overline{DP}_n$. Fluorine content in weight from polystyrene issued from both modes of termination have to be as different as possible in order to differentiate them. The evolution of fluorine content in weight with the $\overline{DP}_n$ for each type of termination shows that the lower $\overline{DP}_n$, the better the difference between the two rates (Figure 1). But low molecular weight determinations may be slightly wrong according to heavy fluorinated end-groups (divergence with regard to standard plot). $\overline{DP}_n$ = 100 seems to be a good compromise.

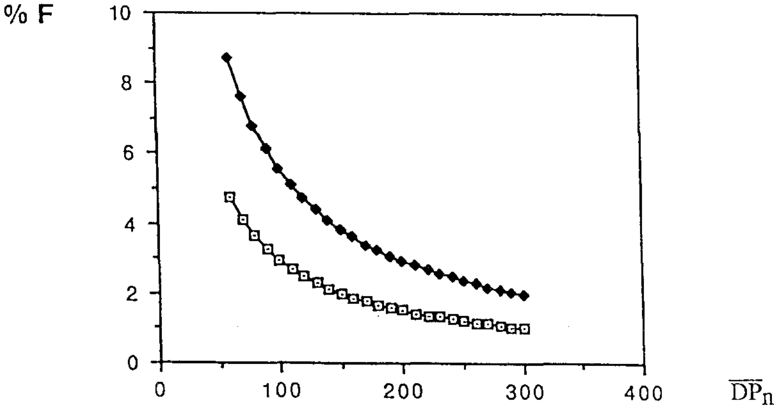


Figure 1: Variation of the fluorine content in weight-% with the number-average degree of polymerization of polystyrene ($\overline{DP}_n$) terminated by recombination (◆), by disproportionation (▣).

There are two possibilities to control the synthesis of this polystyrene: it can operate by concentration or by temperature adjustement. The second way was chosen.

According to Matheson's works (19) on the polymerization of styrene, monomer and initiator concentrations equal to 4,12 mol/L and 4,12 10^{-2} mol/L, respectively were used. In order to find the working temperature "T_2" giving the $(\overline{DP}_n)_{T2}$ =100 expected, a first value of $(\overline{DP}_n)_{T1}$ at T_1 = 60°C is calculated. So, we used simplified Mayo's law considering termination obtained at 100% of combination and all transfer terms equal to zero. (equation 1)

$$\frac{1}{\overline{DP}_n} = \frac{(2\,f k_d)^{1/2}}{(1+a)}\;\frac{k_t^{1/2}}{k_p}\cdot\frac{(I_2)^{1/2}}{(M)} \qquad (1)$$

With k_p = 180,3 L/mol.s (19), k_t = 3,54 10^7 L/mol.s (19), k_d = 3,71 10^{-5} s^{-1} (20), f = 0,61 (21), we find $(\overline{DP}_n)_{T1}$ = 180.

It is well know that $\overline{DP}_n$ is linked to temperature by the following law (equation 2).

$$\ln \frac{(\overline{DP}_n)_{T2}}{(\overline{DP}_n)_{T1}} = \frac{1}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)\left(-E_p+\frac{E_d}{2}+\frac{E_t}{2}\right) \qquad (2)$$

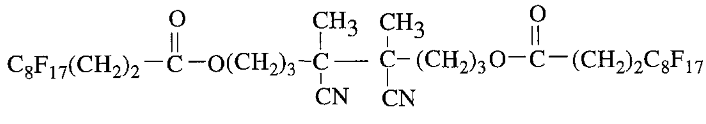
Energetic term is calculated from Matheson's values (19) (E_p= 32,44 kJ/mol, E_t= 9,91 kJ/mol) and from the initiator 1 decomposition activation energy already determined (20) (E_a= 88 kJ/mol).(equation 3)

$$\ln \frac{(\overline{DP}_n)_{T2}}{(\overline{DP}_n)_{T1}} = 1987\left(\frac{1}{T_2}-\frac{1}{T_1}\right) \qquad (3)$$

By replacement of the value $(\overline{DP}_n)_{T1}$ =180 at T_1 = 60°C in the equation 3, it is easy to calculate temperature T_2 which gives 100 expected $(\overline{DP}_n)_{T2}$: T_2 = 96°C.

Styrene polymerization is carried out at this temperature T_2, in solution in toluene (chosen for its low transfert constant).

As we explain previously, our determination of recombination/ disproportionation percentage is based on fluorine content. So, it is necessary to eliminate the remaining initiator and also the by-product obtained from the part of initiator which did not initiate polymerization. Consequently, we have purified three times by precipitation in methanol, the resulting polymer. More over, we have checked by GPC that no peaks appears at high elution volume. Actually, we remain that combination product 5 which appears in negative sens by comparaison with polystyrene, is easily observed by this technique.



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Taking in accound all these requirements, the number-average degree of polymerization of the resulting polystyrene is measured by GPC according to standard polystyrene: $\overline{DP}_n = 98$. The elemental analysis of this same sample gives the fluorine content in weight: %F = 5,9 ± 0,3. This value is close to the fluorine content in weight that would have a polystyrene with a $\overline{DP}_n = 98$ terminated only by recombination (%F = 5,7).

Conclusion

Our study appears to agree with the results obtained by Bamford and Tipper (12): the reaction of termination in styrene polymerization proceeds by combination exclusively. This study can also be considered as a method to calculate the recombination/disproportionation rate.

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