Polymer Bulletin 23, 419–423 (1990)

Polymer Bulletin

Electron spin resonance measurement of nitroxy probes mobility, attached to a polymer through a spacer arm

Alain Guyot[1], André Revillon[1,*], Marcel Camps[2], Jean-Pierre Monthéard[2], and Bernard Catoire[3]

[1]CNRS-LMO, B.P. 24, F-69390 Lyon-Vernaison, France
[2]Université de Saint-Etienne, 23, rue Docteur Michelon, F-42100 Saint-Etienne, France
[3]Institut Textile de France, B.P. 60, F-69132 Ecully Cédex, France

Summary

Stable nitroxide radical probes are attached to styrene-divinylbenzene gel type resins through spacer arms, the length of which being 1 to 7 methylene groups. Results of electron spin resonance analysis which allows to estimate the local viscosity are discussed. Mobility of the nitroxide probes generally increases with the number of CH_2 groups, the effect being compared to a decrease of cross-linking density.

Introduction

It is now well established that a functional group attached to a polymer through a spacer is more active than its homologous directly fixed to the polymer (1,2). One of the proposed explanations is the decrease of steric hindrance when the site is at a greater distance from the surface. This may be true when the support is an inert, non-porous solid, such as silica. The situation is quite different with a polymeric support. The best representation of a swollen crosslinked polymer bead is to consider it as a semi-dilute solution of polymer segments with a variable local viscosity, sometimes very high. The spacer may increase the local mobility of the functional group in the medium, but its mobility remains lower than that of the corresponding unattached molecule. Our approach was to use the spin-labeling technique to evaluate the functional site mobility, in the swollen state, when a stable free radical $NO^{\cdot}$ is attached to it. The rotational correlation time τ, determined from the ESR spectrum is proportional to the internal viscosity. Regen has found that τ decreases when swelling increases, depending on the nature of solvent or when crosslinking density decreases, according to divinylbenzene amount, in the range 2 to 12%, in relation with the mobility of substrates bound to the gel (3,4,5). The purpose of this work is to determine the effect of different length of spacers attached to support of different crosslink density. Moreover the studied samples have a morphology different of Regen's ones.

Experimental

Preparation of monomers

Monomers 2a and 2b

The Grignard compound of vinylbenzylchloride 1 (VBC, commercial mixture 60/40 meta/para) is prepared by slow addition of 15.2 g (0.1M) of VBC in 300 mL of anhydrous ether to 2.5 g of magnesium powder stirred with 20 mL of diethyl ether. After completion of reaction, the

---

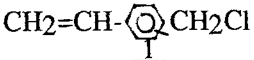
*To whom offprint requests should be sent

Grignard reagent is added to a solution of 21.6 g of 1,4-dibromobutane (0.1 M) -for 2a and 24.4 g of1,4-dibromohexane (O.1 M) for 2b- in 100 mL of tetrahydrofuran with 1mmol of lithium tetrachlorocuprate according to the procedure described by Tomoi et al (2,6). The reaction is allowed to proceed 48 hours instead of 5. The yields are close to 40%.

Monomer 3

Ethylene oxide is reacted with 4-chloromagnesium styrene, then the 4-(2-hydroxyethyl) styrene is treated by triphenylphosphine and carbon tetrachloride, as described in (6).

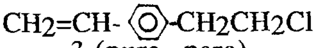
Physical constants (IR and NMR) are in agreement with those described in (7).



1

(meta and para)

2 a) n= 5
b) n= 7



3 (pure para)

Synthesis of polymers

The styrene (St) is a commercial one (Prolabo, 99% purity, 30 ppm t-butyl-4-catechol stabilizer). Divinylbenzene (DVB) is the conventional mixture of 55% pure DVB (isomers % :71 meta, 29 para) and 45% ethylvinylbenzene (EVB) in presence of ~ 600 ppm 2,6-t-butyl-4-methylphenol.

Free-radical copolymerization in suspension is performed at 88°C, under nitrogen, for 8 hrs, with benzoyl peroxide as initiator (1% weight of monomers). The organic phase is diluted (1:1 in volume) by toluene as a solvent porogen. The volume ratio of aqueous phase to organic phase is 5. Stirring rate is 230 rpm. The dispersive agent is the ammonium salt of an alternate styrene-maleic anhydride copolymer (Lytron) in solution 2.5% in water. The protective colloid is an arabic gum, 2% weight in deionised water.

After reaction, the beads are washed with water, then methanol, extracted with methanol in a Soxhlet (~10 cycles) and finally dried at 60°C for 24 hrs under vacuum.

A standard recipe is indicated in Table 1.

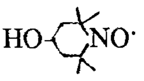
Table 1 - Synthesis of crosslinked terpolymers

Organic phase					Aqueous phase		
Styrene	DVB	VBC	Toluene	BP	H_2O	Lytron	Gum
81 g	12 g	7 g	110 mL	1 g	1 L	25 mL	20 g

Compositions of two series of copolymers are reported in Tables 2 and 3: respectively, constant amount of functional monomer, but varying crosslink density and at constant composition, but varying the number n of methylene groups of spacer from 1 to 7.

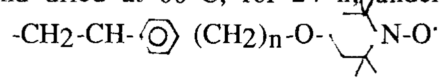
Spin-labelling

The stable free-radical, covalently bound to the support and used as an ESR spin-label is: 4-hydroxy TEMPO or 4-hydroxy 2,2,6,6 tetramethyl piperidinolyoxy,



a commercial product from Aldrich. Sodium hydride is a commercial product from Merck. Dimethylformamide, from Prolabo is distillated before use on CaH_2 under N_2.

6 mg (0.035 mmol) 4-hydroxy TEMPO, 45 mg (1.9 mmol) NaH and 8 mL DMF are stirred under nitrogen at room temperature, for four hours. Then, this mixture is added to 2.3 g (~1 mmol) of support in 75 mL of DMF, for reaction at room temperature, under nitrogen for 24 hours. The support is filtered, successively washed with water, ethanol, benzene, diethyl oxide and dried at 60°C, for 24 h, under vacuum (0.2 tor).



ESR measurements

- Material: The spin-labelled nitroxide polymer powder is swollen in toluene for 24 hours at room temperature and then, without drying, introduced in a quartz tube.

- Equipment: ESR spectra are obtained at 20°C, with a Bruker 100D equipped with a 10000 gauss magnet and working in X band.

Results and discussion

Figure 1 shows the spectra of the polymers including spin-labelled spacers. One can see a well resolved triplet line of 30 gauss total width.

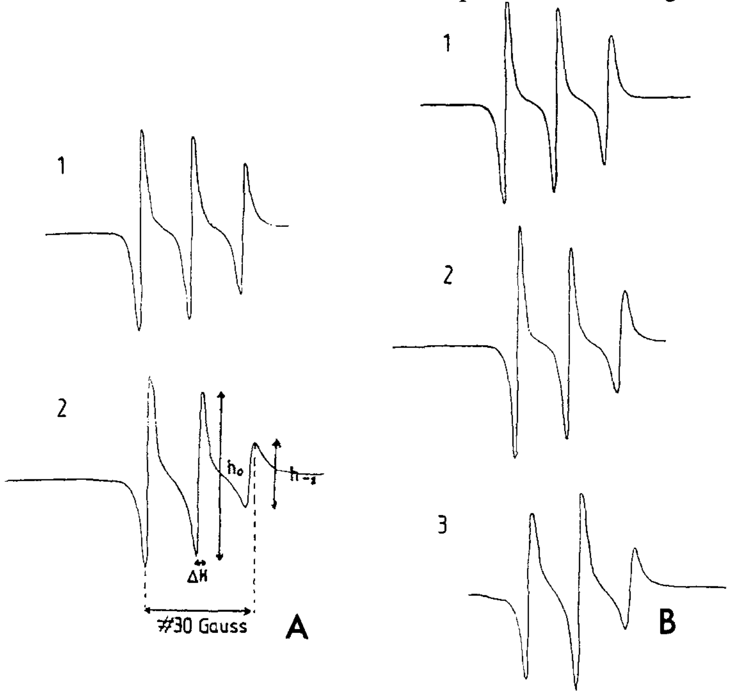


Fig. 1. Room temperature ESR spectra of spin-labelled nitroxide polymers, swollen in toluene: A, as a function of DVB amount 1: 1%; 2: 10% and B, versus the length of the spacer arm: 1:7; 2:5 and 3:1.

However the heights of the high field peaks (-1) are sensitive to the molecular structure Because of the weak anisotropy of spectra due to some difficulty of the spin-labelled spacer to reorientate (10^{-9} - 10^{-10} s), the correlation time is given in this case by

$$\tau\ (s) = 6.5\ 10^{-10}\ \Delta H_0[(\ h_0/\ h_{-1})^{0.5}\ -1]$$

Good reproducibility of τ.mesurements for a series of a given sample has been obtained. Moreover it has been checked that the toluene solution after contacting the polymer and separation from it, does not show any significant signal. It may be concluded that the probe is well attached to the polymer and that the free spin-label is not included in the structure.

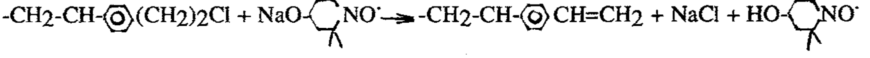
Table 2 - Composition and correlation time for VBC terpolymers

Styrene	93	91	85	75
EVB	1	2	5	10
pure DVB	1	2	5	10
VBC	5	5	5	5
$10^{10}\ \tau$ (s)	3	4	9	9.5

Table 3 - Composition and correlation time for functional spacer terpolymers

Styrene	85	85	85
EVB	5	5	5
pure DVB	5	5	5
Spacer	5	5	5
n and X	1,Cl	5,Br	7,Br
$10^{10}\tau$ (s)	9	6.3	3

The correlation time is proportional to the inner viscosity of the medium. Table 2 shows that for a series where the spacer is short (one methylene group, corresponding to vinylbenzylchloride as starting monomer), this time increases with the amount of crosslinker as already observed by Regen (3). For a series with the same crosslinking density but increasing length n of the spacer arm, the correlation time decreases, as it may be seen in Table 3. This variation is as expected. For this series the effect on τ for n=7 is about the same than a decrease in the amount of crosslinker from 5 to 1%, in the other series. However, the local viscosity has been found very low: $\tau = 0.8\ 10^{-10}$s for the sample where n=2. In that case, the amount of probe attached to the gel was much lower than in the other cases. Two hypotheses may be given: i) the nucleophilic reaction of the sodium salt of the probe may cause the elimination reaction instead of the expected substitution reaction



ii) the spacer arm is ended by a chlorine atom, far less reactive than that of the VBC or than the bromine atom (8) used for longer spacer arms. In all cases, the average extent of derivatization is low (3%), in order to avoid interference effects between NO· groups. It has been found that Br is homogeneously distributed in terpolymers (9), but from our knowledge of the elaboration of morphology, we may assume than a distribution of accessibility of sites exists. Only the more accessible sites by TEMPO give rise to the ESR signal. This may explain that the low value of τ (for n=2) does not correspond to the mean internal viscosity, but to superficial mobility of some functional groups. Two rates of rotational diffusion of the spin labels have been assumed in (10), depending on their attachment on chains on the inner surface or inside zones of higher crosslinking density, for macroporous copolymers. We are going on investigation in this way.

References

1. Tomoi, M., Ogawa, E., Hosokawa, Y., Kakiuchi, H., J. Polym. Sci., Polym. Chem. Ed. 20, 3421 (1982)
2. Tomoi, M., Ogawa, E., Hosokawa, Y., Kakiuchi, H., J. Polym. Sci., Polym. Chem. Ed. 20, 3015 (1982)
3. Regen, S.L., Macromolecules, 8, 689 (1975)
4. Regen, S.L., J. Am. Chem Soc.96:16, 5275 (1974)
5. Regen, S.L., J. Am. Chem Soc.97:11, 3108 (1975)
6. Boinon, B., Benayad, B., Monthéard, J.P., Makromol. Chem. 190, 241 (1989)
7. Braun, D., Keppler, H.G., Makromol. Chem. 78, 100 (1964)
8. Desmurs, J.R., Jouve, I., Gérard, B., Zimmermann, P., L'Actualité Chimique, 121 (1989)
9. Bacquet, M., Lemaguer D., Caze C., Eur. Polym. J. 24, 533 (1988)
10. Pilar,J., Horak, D., Labsky, J., Svec, F., Polymer, 29, 500 (1988)

Accepted January 12, 1990 C