

SYNTHESIS OF POLYSTYRENE-BLOCK-POLYCAPROLACTAM WITH 1,1-BIS-(1'-NAPHTHYL) ETHYLENE AS A DEACTIVATING AGENT

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ABSTRACT

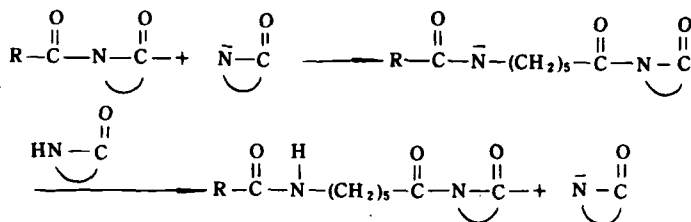
The insertion of 1,1-bis (1'-naphthyl) ethylene monomer unit into the active polystyrene chain end greatly decreased the reactivity of the active chain end to the carbonyl group, and allowed the polymeric chain end to react only with the double bond in N-methacryloyl caprolactam, resulting in N-acylcaprolactam functionalized polystyrene in 100% conversion. New diblock copolymer of polystyrene with polycaprolactam was synthesized by direct reaction of the functionalized polymer with caprolactam without adding additional alkali metal or their caprolactam salts.

INTRODUCTION

Block or graft copolymers have provoked particular interest of polymer blend techniques^[1-9] because these copolymers can reduce interfacial tension, control phase morphology and permit polymer blends to obtain good adhesion of interface. Since these favorable effects occur only in blending different polymers which should be miscible respectively with the different blocks of a copolymer, and polystyrene, polycaprolactam, as well as polymers miscible with them cover a great deal of polymers, it is of interest to synthesize polystyrene-polycaprolactam block copolymer.

This copolymer in principle can be synthesized by the following steps; (i) Preparation of polystyrene initial blocks by anionic polymerization, (ii) Functionalization of the polymer thus obtained, (iii) Extension of the functionalized polystyrene with polycaprolactam blocks.

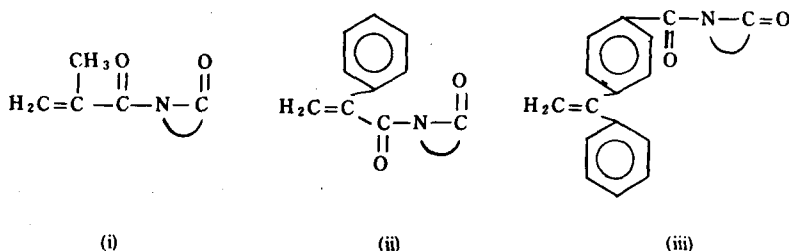
Anionic polymerization of caprolactam has been studied by several investigators^[11-15]. In this polymerization the polymeric chain grows by the addition of caprolactam anions to the carbonyl group of the acylated caprolactam.



The N-acyllactam site at the chain end plays the role of a 'promotor' and it is formed again at the chain end after each step of growth. In the absence of

'promoter', caprolactam itself can initiate polymerization through yielding N-acyllactam sites, but this selfinitiation process is very slow, especially when the temperature remains below 40 °C. Thus, it follows that polystyrene-polycaprolactam block copolymer may be synthesized without formation of caprolactam homopolymer by fitting polystyrene end with a terminal acyllactam function and carrying out the polymerization of caprolactam at low temperature.

The most obvious way to fix a terminal acyllactam function onto a living polymer chain would be to use a vinyl compound which contains an acyllactam function. For example, N-(methacryloyl) caprolactam (i), N-(1-phenylacryloyl) caprolactam (ii), N-[4-(1'-phenylethenyl) benzoyl] caprolactam (iii).



To these compounds if a solution of living polystyrene is directly added, it is apparent that polystyryl anion not only reacts with double bond, but it also effects the nucleophilic addition to the carbonyl group of N-acylcaprolactam. Therefore, thought has to be given to reduce the reactivity of the active site at the chain end to the carbonyl group, but not affect so much the reaction between active site and double bond.

An approach to this idea is to cap polystyryl anion with a vinyl compound which exhibits great steric hindrance to the carbonyl group. Schmitt et al.^[10] employed 1,1-dinaphthylethylene (DPE) as a deactivating agent and synthesized polystyrene-block-polybutyramide. In this paper, the highly deactivating ability of 1,1-bis(1'-naphthyl) ethylene (DNE), the functionalization of the deactivated polystyrene with N-methacryloylcaprolactam as well as the synthesis of polystyrene-block-polycaprolactam are to be described.

EXPERIMENTAL

1. Preparation of 1,1-bis(1'-naphthyl) ethylene

A solution of naphthylmagnesium bromide was prepared in a 1-L three necked, round bottomed flask from 10.9g. (0.45 gram atom) of magnesium turnings, 99.2g. (0.47mole) of 1-bromonaphthalene, 300ml of anhydrous ether and 150ml of dry benzene, according to well known Grignard reaction procedure.

The flask was cooled in an ice bath and a solution of 17.6g. (0.2mole) of anhydrous ethylacetate in 300ml of ether was added dropwise in the course of one hour. Stirring was continued for 50 minute after the addition was finished, and then allowed to stand overnight at room temperature.

The flask was placed in an ice bath, and the contents were decomposed by gradually adding 10ml of saturated ammonium chloride solution.

The ether layer was decanted into a separatory funnel and the pasty residue was extracted with ether. The ether was removed by a Rotavapor and to the residue was added 2g. of KHSO_4 solid. The distillation under high vacuum gave viscous yellowish material. The crude dinaphthylethylene was crystallized from acetic acid and yielded 16.9g. (30.2% based on ethylacetate) of colorless product.

HPLC: Single peak. ^1H NMR(CDCl_3) δ : 5.9(2H, s, $=\text{CH}_2$), 7.4, 7.8, 8.3 (14H, m, naphthalene ring)

2. *Acylcaprolactam-functionalized polystyrene*

Styrene, toluene, and tetrahydrofuran were carefully purified according to well known procedure. In a typical synthesis, 86ml (78.2g) of styrene was polymerized with a sec-butyllithium initiator in 380ml of toluene at 0°C in all-glass sealed reactor by using break seals and standard high-vacuum techniques. After the polymerization was complete, 22ml of polymer solution was taken in order to determine the molecular weight of polystyrene block (GPC $\overline{M}_n = 9.8 \times 10^3$) and the concentration of active chain end. To the remaining solution 2.25g (8.0mmol) of 1,1-bis(1'-naphthyl) ethylene in 43ml of tetrahydrofuran was added with agitation. After crossover reaction was complete (1 day) as monitored by ultraviolet-visible absorption spectroscopy at 434nm, the resulting polymeric 1,1-dinaphthylalkyllithium was reacted at -78°C with 1.8ml (10.4mmol) of N-methacryloylcaprolactam dissolved in tetrahydrofuran. An aliquot was withdrawn for the determination of efficiency of the functionalization.

3. *Polystyrene-block-polycaprolactam*

The above-prepared acyllactam-terminated living polystyrene at -78°C was treated with 97.5g of caprolactam in 400ml of tetrahydrofuran and then warmed to 40°C and maintained at that temperature for 48hrs. The resulted block copolymer was isolated from the mixture by precipitation in methanol.

4. *Characterization*

(1) Functionalized polystyrene

Thin layer chromatography was used in order to determine if there was any unfunctionalized base polymer. Unfunctionalized polystyrene ($R_f=0.80$) can be readily observed and separated from the functionalized polystyrene ($R_f=0.44$) when toluene was used as a mobile phase.

Size exclusion chromatography was used to measure the molecular weight of polystyrene base polymer. After functionalization, the weight per cent of singlet and dimer in sample was estimated according to the area of the GPC curve.

(2) Polystyrene-block-Polycaprolactam

The existence of polystyrene base polymer or polycaprolactam homopolymer in the sample was detected by TLC analysis. Toluene was used as mobile phase when monitoring the existence of polystyrene base polymer ($R_f=0.80$) and/or its functionalized polymer ($R_f=0.44$), and m-cresol was used when determining caprolactam homopolymer ($R_f=0.95$).

Block copolymer was purified by means of extraction of its crude product first with 40% sulfuric acid and then with cyclohexane. Its weight ratio of polycaprolactam

block to polystyrene block was determined from infrared spectroscopy, using the absorption band at 1642cm^{-1} .

RESULTS AND DISCUSSION

1. Functionalization

The results of functionalization of living polystyrene are shown in Table 1. All other experiment conditions are exactly the same except for those items which are specified in Table 1.

Table 1 Functionalization of living polystyrene

Sample no.	Solvent	Funcn. temp.(°C)	Deact. agent	Funcn. agent	Singlet Wt(%)	Dimer (Wt%)
1	BZ	24	DPE	(iii)	78.3	21.7
2	BZ	24	DNE	(iii)	92.9	7.1
3	BZ	24	DPE	(ii)	75.0	25.0
4	BZ	24	DNE	(ii)	85.5	14.5
5	tolu. + THF	-78	DNE	(i)	100	0

DPE: 1,1-diphenylethylene, DNE: 1,1-bis(1'-naphthyl) ethylene, poly (styryl) lithium (PSLi): $\bar{M}_n = 1.25 \times 10^3$, DPE or DNE/PSLi = 1.6

It is believed^[16] that the double bond in compound (iii) can not react with DPE-terminated living polystyrene. Dimers in sample 1 and 2 have to be thought of as the products originated merely from the addition of polymeric carbanion to the carbonyl group in compound (iii). The more reactive the carbanion, the more dimers it gives rise to.

Comparing sample 2 with sample 1, it is easy to be found that DNE is a more powerful deactivator than DPE.

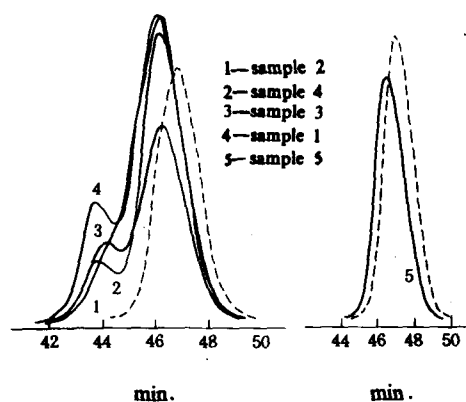


Fig.1 Size exclusion chromatograms of a polystyrene base polymer (---) and of the corresponding functionalized polymer (solid line)

The same effect as above can be observed when the sample 3 is compared with sample 4. However, when the sample 3 and 4 are compared respectively with the sample 1 and 2, the content of dimer in sample 3 or 4 is higher than that in corresponding samples. This increasing dimerization may be attributed to the better reactivity of the double bond in compound (ii), and the reactivity of the double bond in (ii) bears comparison with that of carbonyl group in it.

In order to obtain a highly functionalized polymer, it is necessary to choose a functionalizing agent whose double bond is so much more reactive than carbonyl groups that the reactive chain end can be assumed to react only with the double bond. In N-methacryloylcaprolactam the double bond, which is activated by the nearby electron withdrawing carbonyl groups and its steric hindrance is small, possesses of high reactivity to the active chain end surrounded by voluminous two naphthalene rings and a long polymeric

chain.

Since low temperature helps the steric hindrance to be a main factor of influencing reactivity, and considering those discussed above, the following experiment conditions were chosen: DNE as the deactivating agent; N-methacryloylcaprolactam as a functionalizing agent; and carried out the functionalization reaction at -78°C .

Size exclusion chromatography of this product showed that there was no dimer peak and the curve was symmetrical about center line (Figure 1). In thin-layer chromatography (TLC), no detectable unfunctionalized polymer was found. ^1H NMR spectrum of the functionalized polymer exhibited distinct, characteristic resonances at $\delta=2.55$, 3.86 for the $-\text{CO}-\text{CH}_2-$ and $>\text{N}-\text{CH}_2-$ respectively, which were not present in the ^1H NMR spectrum of the styrene base polymer. Infrared spectrum of the functionalized polymer also indicated the absorption of carbonyl groups at 1650cm^{-1} .

2. Synthesis of polystyrene-block-polycaprolactam

Because the N-methacryloylcaprolactam-terminated polystyrene had been an anion, it was directly treated with purified caprolactam in tetrahydrofuran solution. And the temperature was controlled below 40°C in order to prevent from the formation of caprolactam homopolymer.

In TLC analysis, no detectable polystyrene base polymer and functionalized polymer spots were found. Caprolactam homopolymer spot, however, was detected when m-cresol was used as eluent. The extraction of the copolymer with 40% sulfuric acid showed that the crude copolymer contained 5.4% caprolactam homopolymer, which possibly resulted from the initiation of excess N-methacryloylcaprolactam.

CONCLUSION

1,1-bis (1'-naphthyl) ethylene has better deactivating ability than 1,1-diphenylethylene. The acyllactam-functionalized polystyrene can be synthesized in 100% conversion by reacting poly styryl lithium with 1,1-bis (1'-naphthyl) ethylene and then with N-methacryloylcaprolactam at -78°C . From this functionalized polymer, polystyrene-block-polycaprolactam can be synthesized by anionic polymerization of caprolactam without adding additional alkali metal or its caprolactam salts. The conversion of caprolactam is high and the weight ratio of polycaprolactam to polystyrene was estimated to be 1.48.

Keywords:

1,1-bis (1'-naphthyl) ethylene; N-methacryloylcaprolactam; Polystyryllithium; Polystyrene-block-polycaprolactam

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