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Synthesis of graft copolymers by ring-opening polymerization of 2-nonyl- and 2-phenyl-2-oxazoline initiated by macroinitiators containing benzylchloride functions

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Summary

Graft copolymers with poly(2-nonyl-2-oxazoline) and poly(2-phenyl-2-oxazoline) graft arms have been synthesized using the "grafting from" method. Slightly branched statistical copolymers of isobutene and (m,p)-chloromethylstyrene, synthesized cationically, as well as linear homo-poly((m,p-chloromethylstyrene) have been used as macroinitiators for the ring-opening polymerization of the substituted oxazolines. The graft copolymerizations were carried out in bulk and in benzonitrile solutions with and without addition of potassium iodide. The influence of the reaction conditions on the rate of polymerization and the different reactivities of 2-nonyl-2-oxazoline and 2-phenyl-2-oxazoline were discussed.

Introduction

The cationic ring-opening polymerization of different 2-substituted oxazolines with the focus on ethyl and methyl substituted derivatives is well known (1), especially since they can act as precursors for linear poly(ethyleneimine). In addition, the living character of this polymerization and thus, the possibility to control the molar masses and to synthesize telechelics and macromonomers, the insensitivity towards impurities like water, and the reaction temperatures above room temperature further increased the interest in this polymer class even in industry (1-3). Poly(2-nonyl-2-oxazoline), e.g., has been studied as a model for polymers based on fatty alkyl-2-oxazolines (3).

The synthesis and copolymerization of macromonomers based on 2-phenyl-2-oxazoline leading to graft copolymers (4) was studied in detail in our group. Graft copolymers with poly(oxazoline) graft arms can also be obtained via "grafting onto" (5) and "grafting from" (6). In the latter e.g. the macroinitiator was obtained from polystyrene and subsequent partial chloromethylation of the aromatic unit. The resulting chloromethylstyrene units functioned as initiating sites for the ring opening polymerization of 2-methyl-2-oxazoline (6). The very versatile macroinitiator route to graft copolymers with oxazoline groups was also followed by Dworak (7) who initiated the cationic polymerization of 2-methyl- and 2-phenyl-2-oxazoline with an acid chloride group containing macroinitiator.

Recently we reported the cationic copolymerization of isobutene and (m,p)-chloromethylstyrene and the use of these copolymers as macroinitiators for the polymerization of 2-methyl-2-oxazoline (8). Highly amphiphilic graft copolymers were obtained by this method and their subsequent hydrolysis and quaternization with methyliodide resulted in a new type of polyelectrolyte (9). We used now these macroinitiators for the synthesis of graft copolymers with poly(2-phenyl-2-oxazoline) and poly(2-nonyl-2-oxazoline) graft arms, two oxazoline derivatives with very different reactivity.

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Experimental part

Materials

2-Phenyl-2-oxazoline (PhOxa) (Aldrich, Steinheim, Germany) and 2-nonyl-2-oxazoline (NoOxa) (Henkel KGaA, Düsseldorf, Germany) were stirred over KOH pellets at 50°C for 4 hours, filtered off and bidestilled over CaH_2 under vacuum (b.p. 75 °C/ 0,1 mbar and 80 °C/ 0,2 mbar, respectively) and stored over dry nitrogen. KI was obtained from Aldrich and used as received. The syntheses of the macroinitiators poly(isobutene-*co*-chloromethylstyrene) **MI1** with 58 mol% (m,p)-chloromethylstyrene (CMS) ($\overline{M}_n$ = 7400 g/mol, $\overline{M}_w/\overline{M}_n$ = 2.1) and **MI2** with 27 mol% CMS ($\overline{M}_n$ = 16300 g/mol, $\overline{M}_w/\overline{M}_n$ = 2.3) have been described previously (8). Linear poly((m,p)-chloromethylstyrene) **MI3** ($\overline{M}_n$ = 21200 g/mol, $\overline{M}_w/\overline{M}_n$=2.87) was synthesized via free radical polymerization using AIBN as initiator according to the literature (10). All solvents were bidestilled before use.

Instruments

NMR spectra were taken with a Bruker ARX 300 (resonance frequencies: 300 MHz for ^1H and 75.5 MHz for ^{13}C). A Bruker IFS 55 was used for the FT-IR measurements in KBr and chloroform solution. The UV/VIS spectra were taken with a Varian Cary 3. A Waters system (pump 510, UV detector 486, RI detector 410, ultrastyragel 7 µm columns (500, 10^3, 10^4, 10^5)) with THF as eluent at a flow rate of 0.5 mL/min and calibrated with polystyrene standards was applied for GPC measurements. Elemental analyses were carried out in the laboratories of organic and inorganic chemistry of the Technical University Munich. Thermogravimetric analysis (STA) were performed under nitrogen atmosphere (heating rate = 10°C/min) with a Polymer Laboratories STA1500.

*Synthesis of Graft Copolymers **GP1, GP2 and GP3***

The graft copolymerizations were carried out in solution and in bulk for **GP1** (poly(isobutene-*co*-(m,p)-chloromethylstyrene)-*g*-2-nonyl-2-oxazoline))and**GP3**(poly((m,p)-chloromethylstyrene-*g*-2-nonyl-2-oxazoline)). **GP2** (poly(isobutene-*co*-(m,p)-chloromethylstyrene)-*g*-2-phenyl-2-oxazoline)) was synthesized mainly in bulk.

Experiment in solution (compare Table 1) :

In a typical experiment (**GP1c**) 0.10 g of **MI1** (0.518 mmol initiator functions), 10 mL of benzonitrile, and 2.7 g (13.7 mmol) of 2-nonyl-2-oxazoline were placed under dry nitrogen in a glass tube and stirred at 150°C for 72h. After the polymerization was completed, benzonitrile and unreacted monomer were removed in vacuum at 80 °C and the product was purified through a exhaustive extraction with acetonitrile. Yield: 2.25g (80.4%). The experiments with 2-phenyl-2-oxazoline were performed similarly but the purification was carried out by precipitation in diethyl ether.

Experiment in bulk (compare Table 1 and 2):

In a typical experiment (**GP1a**) 0.050 g of macroinitiator **MI1** (0.259 mmol initiator functions) and 13.5 g (68.4 mmol) of 2-nonyl-2-oxazoline were placed under dry nitrogen in a glass tube and stirred at 150°C for 48 h. The product was purified by extraction as described above. Yield: 1.28g (9.4 %). The polymerization with PhOxa was carried out similarly at 170 °C with a work-up procedure as described above.

Experiments for the conversion/time evaluation (with and without KI, compare Fig.1)

For the results given in Fig.1 0.10 g **MI2** (0.33 mmol initiator functions) were dissolved in a mixture of 7 mL benzonitrile and 3 mL dimethylformamide (necessary to dissolve KI). With KI: 0.055 g KI (0.33mmol) were added. After the addition of 3.35 g (22.7 mmol) PhOxa or 2.25 g (11.4 mmol) NoOxa, respectively, the reaction was carried out for different reaction times at 150 °C. The products were purified as described above and the conversion of the graft monomer was determined.

Characterization (typical examples):

GP1b:

^{1}H NMR ($CDCl_3$, δ in ppm): signals of the graft arms: 0.85 (t, CH_3, n), 1.26 (m, CH_2, m), 1.59 (m, CH_2, l), 2.1-2.5 (m, CH_2, k), 3.44 (m, CH_2, h,i), 4.4 (broad, CH_2, g); signals of isobutene units: 1.10 (s, CH_3, d), 1.41 (s, CH_2, c), in addition very weak and broad: 6.5 - 7.5 (H_{ar}, f, CMS units)

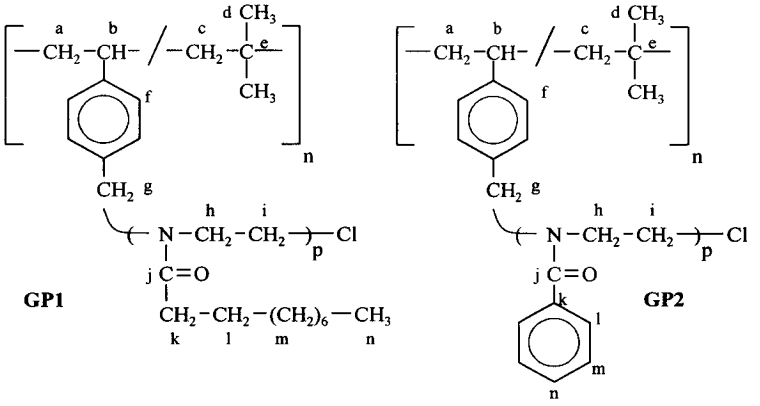
^{13}C NMR ($CDCl_3$, δ in ppm) = 14.1 (n), 25.3 (l), 22.6, 29.3, 29.5, 31.8 (m), 32.9 (k), 42.0 - 48.0 (m, CH_2,g,h,i), 173 (CO, j); 30.9 (d), 38.1 (e), 59.5 (c) (isobutene units); signals a,b,f too weak.

GP2a:

^{1}H NMR ($CDCl_3$, δ in ppm): signals of the graft arms: 2.5-4.0 (m, broad, CH_2, h,i), 4.5 (broad, CH_2, g), 6.5-7.6 (m, H_{ar}, k-n); signals of the isobutene units: 1.1 (s, CH_3, d), 1.41 (s, CH_2, c); signals of CMS units (a,b,f) overlapped by the oxazoline signals.

^{13}C NMR ($CDCl_3$, δ in ppm): 41.0-49.0 (CH_2,g,h,i), 126.4, 128.5, 129.7, 135.7 (C_{ar}, k-n), 172 (CO, j); 30.9 (d), 38.1 (e), 59.5 (c) (isobutene units), signals a,b,f too weak.

GP3a: identical to **GP1a**, however without the signals for the isobutene units.



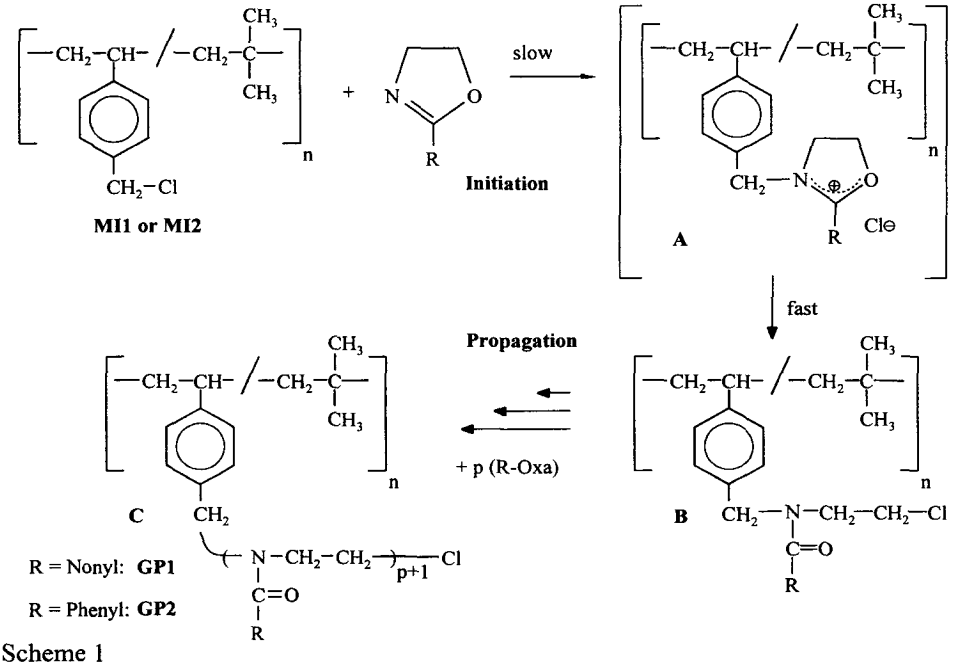
Results and discussion

Three macroinitiators **MI1**, **MI2**, and **MI3** with different amounts of chloromethylstyrene units were used in the described experiments for the synthesis of graft copolymers. The statistical copolymers of isobutene and (m,p)-chloromethylstyrene (CMS) (**MI1** and **MI2**) were synthesized via cationic polymerization as described previously (8) and were obtained with $\overline{M}_n$ of 7400 and 16300 g/mol and a content of aryl-CH_2Cl groups of 58 and 27 mol%, respectively. As already was discussed (8), **MI1** and **MI2** are slightly branched polymers due to the fact that (m,p)-chloromethylstyrene (CMS) can act simultaneously as monomer and as initiator in the cationic polymerization. The linear homopolymer of (m,p)-chloromethylstyrene (**MI3**) ($\overline{M}_n$ = 21200 g/mol) was synthesized through free radical polymerization as reported in the literature (10).

The benzylchloride groups in these polymers can initiate the polymerization of 2-oxazolines (11). This fact was used for the synthesis of graft copolymers via ring-opening cationic polymerization of 2-nonyl- and 2-phenyl-2-oxazoline (NoOxa and PhOxa, respectively) according to the "grafting from" method as shown in Scheme 1 for **GP1** and **GP2**. Similarly, the homopolymer **MI3** was grafted with NoOxa leading to **GP3**. The polymerizations were carried out at 150 or 170 °C in benzonitrile solution and in bulk. Bulk polymerization was possible because the macroinitiators were soluble in the applied oxazoline monomers. By thermal analysis, GPC, and NMR studies it was verified that the macroinitiators

MI1, **MI2**, and **MI3** are thermally stable under these reaction conditions. On the other hand, the blank experiments in Table 1 and 2 proved that under the given reaction conditions but in the absence of any macroinitiator no polymerization of the oxazoline monomers occurred. The reaction conditions and the results are summarized in Table 1 and 2.

From the results in Table 1 and 2 it can be seen that the polymerization of NoOxa (**GP1**, **GP3**) and PhOxa (**GP2**) is very slow even at reaction temperatures of 150 °C and higher. This is typical for the covalent mechanism which is proposed for the polymerization of oxazolines initiated by benzylchloride functions (11). In both, the initiation and the propagation step, a transient oxazolinium salt such as intermediate **A** must be involved (Scheme 1). However, **A** rearranges quickly to the covalent species **B** because of the larger nucleophilicity of the $Cl^{\ominus}$ anion compared to NoOxa or PhOxa. Therefore, the propagating species in the ring-opening polymerization of the NoOxa and PhOxa initiated by the macroinitiators **MI1**, **MI2**, and **MI3** are covalently bound alkyl chloride species such as **B** or **C**. A strong difference in reactivity dependent on the amount of initiating sites in the used macroinitiators could not be found.



Scheme 1

PhOxa is known to be a monomer of low reactivity. This was verified in our experiments: at 150 °C in solution no reasonable amount of graft copolymer could be isolated (compare Fig.1) and therefore, it was necessary to carry out the reaction in bulk at 170 °C. Even then, only an average $\overline{P}_n$ of 9 was achieved for the graft arms in **GP2**. NoOxa is more reactive, especially in solution (up to 80% yield and $\overline{P}_n$ of the graft arms up to 63), but still, reaction times of up to 72 h were required. A direct analysis of the molar masses of the branched graft copolymers or the graft arms was not possible. Therefore, the polymerization degree $\overline{P}_n$ of the graft arms was calculated based on the yield and on the assumption that all initiating sites of the macroinitiators were effective. The nitrogen content found in the graft products agreed well with the calculated values based on this theoretical $\overline{P}_n$.

Table 1: Graft copolymerization of 2-nonyl-2-oxazoline in benzonitrile (10 mL) solution and in bulk without KI: experimental details and results ($\overline{P}_n$ of the graft arms calculated from the yield, N = nitrogen content in the polymer by elemental analysis (found) and calculated based on $\overline{P}_n$)

GP	MI	[MI] in g	[NoOxa] in g	Reaction time in h	Yield in %	$\overline{P}_n$ graft arm	N in % calc.	found
in bulk at 150°C								
GP1a	**MI1**	0.05	13.5	48	9.4	24	6.81	6.97
GP1b	**MI2**	0.06	9.0	72	21.2	48	6.87	6.90
GP3a	**MI3**	0.05	13.5	72	30.3	63	7.02	7.04
blank	-	-	9.0	72	0	-	-	-
in benzonitrile solution at 150°C								
GP1c	**MI1**	0.1	2.7	72	80.4	21	6.76	6.70
GP3b	**MI3**	0.1	2.7	72	76.4	16	6.80	6.90

Table 2: Graft copolymerization of 2-phenyl-2-oxazoline in bulk at 170°C without KI: experimental details and results ($\overline{P}_n$ of the graft arms calculated from the yield, N = nitrogen content in the polymer by elemental analysis (found) and calculated based on $\overline{P}_n$)

GP	MI	[MI] in g	[PhOxa] in g	Reaction time in h	Yield in %	$\overline{P}_n$ graft arm	N in % calc.	found
GP2a	**MI2**	1.5	34	14	9.8	3	5.52	5.87
GP2b	**MI2**	3.0	67	26	18.7	7	7.26	7.80
GP2c	**MI2**	5.1	95	32	27.4	9	7.67	8.02
blank	-	-	30	48	0	-	-	-

The selective solubility behavior (Table 3) of the macroinitiators, the graft copolymers and the homopolymers of the oxazoline monomers (13) allowed to fractionate the reaction product in these three components and thus, to determine the graft success (% of macroinitiatior which is grafted) and the graft yield (= % graft copolymer in the overall product yield; the product yields are given in Table 1 and 2). The macroinitiators **MI1** and **MI3** are soluble in ethyl acetate whereas the corresponding graft copolymers obtained with NoOxa are not. When the polymerization product of NoOxa from **MI1** (or **MI3)** was extracted with ethyl acetate for 24 h no macroinitiator could be isolated in the filtrate (Schema 2). Similar results were obtained with the polymerization product of NoOxa from **MI2** when it was treated with diethyl ether. This fact demonstrates that the incorporation of the macroinitiators in the graft copolymer is quantitative and thus, the graft success has to be 100%. Further extraction of the reaction product with acetonitrile at 70 °C allows to distinguish between homo-poly(2-nonyl-2-oxazoline) and the graft product since only the homopolymer is soluble in this solvent (13). Since no homo-poly(2-nonyl-2-oxazoline) could be detected in the extract the graft yield has to be also 100%, meaning no chain transfer reaction to the monomer took place.

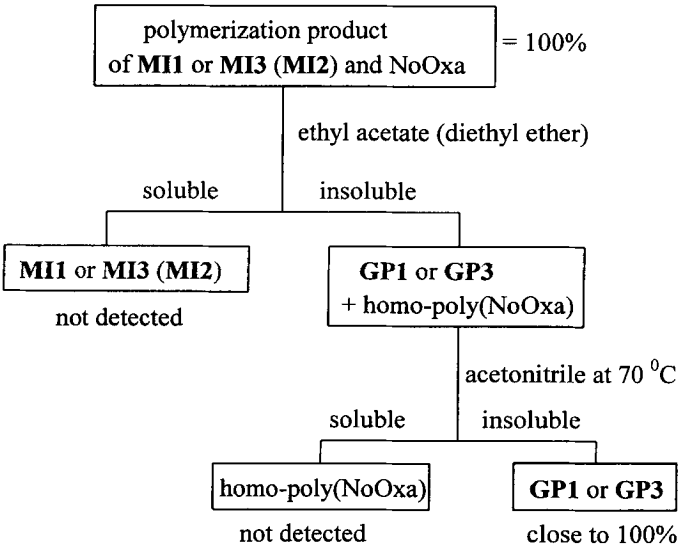
The polymerization product of the PhOxa from **MI2** was analyzed similarly using the fact that the macroinitiator **MI2** is soluble in toluene but the graft copolymer **GP2** is insoluble in this solvent. Again, a 100% graft success could be verified. Due to the large excess of graft monomer used in our experiments compared to the amount of macroinitiator high degrees of

grafting (% polymer formed by the graft monomer in the product) were obtained: above 99% for the NoOXA graft products and about 83 % for the PhOXA graft products. Therefore, it is surprising that the solubility behavior of the graft products **GP1** and **GP3** still differs from that of homo-NoOXA.

Table 3: Qualitative solubility behavior at room temperature of the macroinitiators **MI**, the graft copolymers **GP**, and for comparison, of homo-poly(2-phenyl-2-oxazoline) PPhOxa and homo-poly(2-nonyl-oxazoline) PNoOxa (S = soluble, I = insoluble; 10 wt% solutions).

Solvent	**MI1**	**MI2**	**MI3**	**GP1/GP3**	**GP2**	PNoOxa	PPhOxa
Ethyl acetate	S	I	S	I	I	I	I
Acetonitrile	I	I	I	I	S	S[1]	S
Diethyl ether	I	S	I	I	I	I	I
Toluene	S	S	S	S	I	S	I

[1] soluble only at 70 °C



Scheme 2

The proposed structure for these polymers (Scheme 1) is supported by NMR spectra (compare experimental part). ^{1}H NMR signals for the backbone (e.g. at 1.1. and 1.4 ppm for isobutene units) are weak but clearly detectable in **GP1** and **GP2** as long as the molar excess of the graft arms is not too large. The FT-IR spectra of the graft copolymers show a strong absorption band of the amide carbonyl groups ($\nu_{c=0}$ at 1634 cm^{-1}) and the UV spectra give an additional confirmation of the presence of **MI** in the graft copolymers for **GP1** and **GP3** since the absorptions of aromatic rings at 250 nm from the chloromethylstyrene (CMS) units can be detected. For **GP2** the UV absorption of the CMS units is overlapped by that of the aromatic units of the graft arms.

It is believed that the cationic ring-opening polymerization of 2-oxazolines is mainly governed by two factors, namely, the ring-opening reactivity of the propagating oxazolinium species and the nucleophilicity of the monomer (2,13-15). Since the propagation in our case

occurs via a covalent mechanism, the second factor, the monomer nucleophilicity, dominates. NoOxa has a larger nucleophilicity than PhOxa (4) and therefore, a larger polymerization rate is expected for NoOxa. This is confirmed by the experimental results (Table 1 and 2).

The addition of KI to the graft reaction increased dramatically the polymerization rate for both, NoOxa and PhOxa, as shown in Fig.1. This effect is well known and is attributed to a change in the nature of the propagating species from a covalent alkyl chloride (intermediate **B**, Scheme 1) to an ionic oxazolinium iodide (compare intermediate **A** in Scheme 1) (2). It is believed that an exchange reaction of chloride with iodide takes place between aryl-CH_2Cl and KI and or between the propagating species **C** and KI (2). Since the nucleophilicity of most oxazoline monomers is higher than that of the iodide counterion, the ionic oxazolinium species is favored in the propagation step and the polymerization rate is now not only governed by nucleophilicity of the oxazoline monomer but also by the ring-opening reactivity of the propagating species. In earlier studies (15) it was found that the ring-opening reactivity of the phenyl oxazolinium ion is higher than that of the methyl oxazolinium ion, but due to the higher nucleophilicity of the latter, overall a higher polymerization rate were observed for MeOxa. Similarly, in our studies on PhOxa and NoOxa, a much higher polymerization rate for NoOxa was found when trifluoromethanesulfonic acid methyl ester was used as initiator (13) which leads to an exclusive ionic polymerization mechanism. The graft experiments in the presence of KI confirm these results. The polymerization rate k_p for NoOxa initiated by **MI1** is about 18 times that of PhOxa (116×10^{-4} and 6.3×10^{-4} $Lmol^{-1}s^{-1}$, respectively) and thus, even in the presence of KI, the polymerization of PhOxa is still dominated by its low nucleophilicity which is even lower than that of iodide (2). This might be an indication for a still partially covalent mechanism.

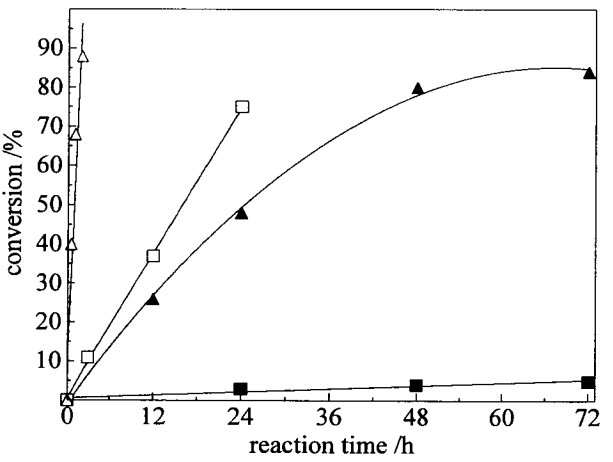


Fig.1: Graft monomer conversion versus reaction time for the graft reaction initated by **MI2** at 150 °C in benzonitrile /dimethylformamide solution using
PhOxa (■) without KI
PhOxa (□) with KI
NoOxa (▲) without KI
NoOxa (Δ) with KI

The graft copolymers synthesized via "cationic grafting from" with poly(2-phenyl-2-oxazoline) and, for the first time, with poly(2-nonyl-2-oxazoline) graft arms led to very interesting materials which might find application as compatibilizers in blends. In addition, the high flexibility of the "grafting from" method in the number and length of the graft arms in combination with the special "living" character of the polymerization of oxazolines offers the possibility to further optimize the properties of the graft copolymers.

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