



Synthesis of Novel Plasticizers Based on Poly(ϵ -caprolactone) and a Consideration of Their Influence on Nitroglycerine Migration in Double Base Solid Propellants

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Abstract: The presence of nitroglycerine (NG) in double base propellants and its subsequent migration from the propellant towards the inhibitor has always been an important issue. This problem may be considerably reduced by exploiting the concept of the introduction of electron donor sites to the propellant formulation. Plasticizers based on ϵ -caprolactone (ϵ -CL) were synthesized and characterized, and their activities for absorbing nitroglycerine were investigated. According to the results, the order of NG absorption is: PCL-(OH)₂ < PCL-(OH)₃ < PCL-(OH)₄ < H-PCL. The observed differences in the properties of the plasticizers is discussed in terms of structural considerations. The data also showed that the hyperbranched poly(ϵ -caprolactone) (H-PCL) has the greatest effect in decreasing NG migration. Furthermore, the activity of these plasticizers in decreasing NG migration was also investigated by IR analysis.

Keywords: nitroglycerine, double base propellants, migration, ϵ -caprolactone, plasticizer

1 Introduction

In double base (DB) propellants consisting of nitroglycerine (NG) and nitrocellulose (NC), a number of chemical and physical processes, such as expenditure of stabilizer, migration and evaporation of NG, decomposition of NG and NC, *etc.* occur within the grains. All of these processes can decrease the performance of the propellants [1]. Since NG migrates from the propellant

towards the inhibitor, the inhibiting materials for double base rocket propellants should be selected carefully [2-4]. The extent of NG migration is one of the most important factors that should be considered. Although slight migration of NG is commonly useful for the adhesive bond, migration to a larger extent can lead to a number of problems. Following excessive NG migration, the performance decreases and, simultaneously, combustion increases. Large NG migration cannot only cause swelling and delamination of the inhibitor, but also leads to the inhibitor being mechanically weak and soft [4-6]. This process results in coning of the burning propellant, particularly in an end-burning propellant [7]. These problems are severe and several physical and chemical methods have been developed to minimize them by diminishing NG migration [2, 8].

Several concepts have been reported to prevent/reduce the extent of NG migration [6]. In this regard, one of the most important is the attraction force concept, which represents an electrostatic attraction between NG and the inhibitors, leading to NG migration [9].

Application of some types of polymers, having a loose structure, as inhibitors for propellants has been frequently reported. NG, due to its small size, can easily penetrate the structure of these polymers; so, the addition of fillers to the polymers could be a reasonable solution to this issue. On the other hand, the ability of NG molecules to diffuse into polymers is significantly decreased by application of denser nets [10-12]. Crosslinking (thermosets) or a high degree of crystallinity (linear thermoplastics) result in diminished mobility of the polymer chains [13, 14].

Changes in nitroglycerine content significantly affects the mechanical properties of a propellant. This is one reason why nitroglycerine evaporation and migration from double base propellants has become a very important issue. Different methods to prevent plasticizer migration from propellants have been suggested. Even though changes to the surface can reduce plasticizer migration to the surface to some extent, it is never able to stop their movement from matrix towards the surface, and it only prevents them from remaining on the surface. Therefore, random dispersion of plasticizers in a propellant matrix, which originates from migration, will still exist after surface modification, and disrupts a propellant's good specification and causes its burning to become unsteady. Hence, introducing a new procedure for reducing migration based on modification of a propellant's matrix is necessary. Thus, the main purpose of this research was to prevent NG migration by modifying the matrix of an NC-NG propellant. One of the proposed methods for reducing NG migration was to add some types of ester and polyester plasticizers which are able to function as both additive and plasticizer components. For this purpose, different plasticizers

were synthesized and characterized. Their performances were then considered for reducing NG migration.

2 Materials and Methods

All reagents and solvents used in this study are commercially available and were purchased from commercial suppliers (Acros, Merck and Aldrich), with the exceptions of NC and NG samples, which were kindly provided by defence industries (Ministry of National Defence, Iran), and had high purity. The FT-IR absorption spectra were run on a spectrophotometer (Nicolet 800) as KBr pellets. Vibrational transition frequencies were reported in wave number (cm^{-1}). Poly(ϵ -caprolactone) diol (PCL-(OH)₂) was an industrial sample with $M_n = 2000 \text{ g}\cdot\text{mol}^{-1}$. The double-base (DB) propellants were prepared by the casting technique.

3 Experimental

3.1 Synthesis of plasticizers

The synthesis of the plasticizers were carried out by a one-step polyesterification process. A typical procedure for the polymerization was as follows: a 50 mL round-bottomed flask, equipped with a magnetic stir bar, was charged with ϵ -caprolactone (ϵ -CL) (5 g, 4.8 mL, 44 mmol), glycerol (0.34 g, 0.27 mL, 3.7 mmol) and dibutyltin dilaurate (0.031 g, 0.05 mmol). The reaction mixture was stirred under a nitrogen atmosphere at 120 °C for 24 h. After cooling the reaction mixture, it was diluted with CH_2Cl_2 (10 mL) and then cold *n*-hexane (15 mL) was added to precipitate a white solid. By decanting the solvent, the precipitate was isolated, washed with additional cold *n*-hexane and air-dried. This polyester was designated as PCL-(OH)₃. The monomer conversion was determined directly from IR measurements of the polymerization mixtures. FT-IR (KBr, cm^{-1}): $\nu = 3432$ (OH, stretching), 2964, 2943 (C–H, stretching, aliphatic), 1724 (CO, stretching), 1194 (C–O, stretching), 733 (CH_2 , bending). ¹H NMR (300 MHz, ppm, CDCl_3): $\delta = 4.06$ (t, 2H, COOCH_2), 2.33 (t, 2H, CH_2CO), 1.68–1.62 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 1.44–1.34 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$).

The plasticizer poly(ϵ -caprolactone) tetraol (PCL-(OH)₄) was also synthesized using the same procedure. FT-IR (KBr, cm^{-1}): $\nu =$ FT-IR (KBr, cm^{-1}): $\nu = 3482$ (OH, stretching), 2939, 2867 (C–H, stretching, aliphatic), 1732 (C=O, stretching), 1245, 1168 (C–O, stretching), 762 (CH_2 , bending). ¹H NMR

(500 MHz, CDCl_3): δ (ppm) = 4.07 (t, 2H, COOCH_2), 2.31 (t, 2H, CH_2CO), 1.66-1.62 (m, 4H, $\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$), 1.41-1.36 (m, 2H, $\text{OCH}_2\text{CH}_2\text{CH}_2$).

3.2 Synthesis of dendrimer initiator

Isopropylidene-2,2-bis(methoxy)propionic acid (1) [15]. 2,2-Bis(hydroxymethyl)propionic acid (bis-MPA) (3 g, 22 mmol), 2,2-dimethoxypropane (3.4 g, 4 mL, 32.6 mmol) and *p*-toluenesulfonic acid monohydrate (0.21 g, 1.1 mmol) were dissolved in acetone (25 mL). The reaction mixture was stirred for 4 h at room temperature. A solution of NH_3/EtOH (1:1; 0.3 mL) was then added to neutralize the catalyst. The solvent was removed at room temperature. The raw product was dissolved in dichloromethane (10 mL) and was washed with distilled water (2×10 mL). The organic phase was dried over magnesium sulfate and concentrated to give isopropylidene-2,2-bis(methoxy)propionic acid (55% yield) as white crystals; mp: 127-131 °C. FT-IR (KBr, cm^{-1}): $\nu = 3432, 2994, 1720, 1261, 1072$. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 4.17, 3.65 (4H, $-\text{CH}_2\text{OC}(\text{CH}_3)_2\text{OCH}_2$), 1.41, 1.37 (6H, $\text{CH}_2\text{OC}(\text{CH}_3)_2\text{OCH}_2$), 1.20 (3H, $\text{CH}_3\text{C}(\text{CH}_2\text{O})_2\text{COOH}$).

Esterification of isopropylidene-2,2-bis(methoxy)propionic acid and pentaerythritol (2) [16]. Isopropylidene-2,2-bis(methoxy)propionic acid (1.8 g, 10.3 mmol) and pentaerythritol (0.33 g, 2.4 mmol) with 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DPTS) (0.57 g, 1.95 mmol) were mixed in dichloromethane (10 mL) under an argon atmosphere. Dicyclohexylcarbodiimide (DCC) (2.5 g, 12.1 mmol) was then added and the reaction mixture was stirred at room temperature for 15 h. The substituted urea and unused catalyst were removed by filtration and washed with a small volume of dichloromethane. The solvent was evaporated to give the product (3.8 g, 48% yield) as a white solid; mp: 129-133 °C. FT-IR (KBr, cm^{-1}): $\nu = 2929, 1726, 1259, 1076$. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ (ppm) = 4.25 (8H, CH_2OCO), 4.17, 3.65 (8H, CH_2O), 1.41 (12H, CH_3), 1.35 (12H, CH_3), 1.15 (12H, CH_3).

Removal of the acetonide protective group from ester (3) [15, 16]. The synthesized ester (3) (3.8 g, 5 mmol) was dissolved in dry methanol (45 mL). Amberlite resin (1 g) was then added and the reaction mixture was stirred for 3 h at room temperature. After completion of the reaction, the resin was separated from the reaction mixture and washed with methanol. The solvent was evaporated to give 4 (3.2 g, 73% yield) as white crystals; mp: 134-141 °C. FT-IR (KBr, cm^{-1}): $\nu = 3323$ (O-H, stretching), 2927 (C-H, stretching), 1726 (C=O, stretching) 1218, 1083 (C-O, stretching).

The hyperbranched poly(ϵ -caprolactone) (H-PCL) was synthesized using the same procedure. FT-IR (KBr, cm^{-1}): $\nu = 3321$ (OH, stretching), 2935, 2864

(C–H, stretching, aliphatic), 1722 (C=O, stretching), 1164 (C–O, stretching), 731 (CH₂, bending). ¹H NMR (500 MHz, CDCl₃): δ (ppm) = 4.05 (t, 2H, COOCH₂), 2.30 (t, 2H, CH₂CO), 1.67-1.61 (m, 4H, OCH₂CH₂CH₂CH₂), 1.40-1.36 (m, 2H, OCH₂CH₂CH₂).

The details of the formulations of these plasticizers are shown in Table 1. These polyesters were characterized by IR and ¹H NMR spectroscopy.

Table 1. Composition (mmol) of plasticizers

Plasticizer	Initiator	ε-Caprolactone	Catalyst	[M] ₀ /[I] ₀ ^a	M _w [g/mol]
PCL-(OH) ₃	3.7	44	0.05	12/1	3165
PCL-(OH) ₄	0.73	13.14	0.018	18/1	3436
H-PCL	0.83	26	0.031	32/1	3758

^a Ratio of [-CL]/[alcohol]

3.3 Investigation of nitroglycerine migration in double base propellants

Different methods have been reported to study the migration rate of a plasticizer in a polymer matrix. In this investigation, with due attention to the available facilities, the Sandwich Test method was used for studying nitroglycerine migration in double base solid propellants [17-19].

3.3.1 Preparation of sample for the Sandwich Test

To prepare the test samples, ethyl cellulose (1 g) was dissolved in dichloromethane (25 mL) and stirred for 2 h at room temperature. 5 wt.% of the synthesized plasticizer was then added to the viscous solution and stirred at room temperature for 2 h. The viscous solution was poured into the moulds prepared to achieve the desired thickness. After evaporating the dichloromethane, the samples were cut to form the desired discs, 10±1 mm diameter and 0.2 mm thickness. The discs' surface must be free of any pollution and the samples thickness should be even.

3.3.2 Test method

After achieving the test fulfillment conditions, the test samples were weighed as discs with 0.001 g accuracy, and average thickness of 0.02 mm. The test samples were placed between two fuel layers so that they had coincident axes and constituted a sandwich. They were then placed between two glass sheets. A weight was placed on the fuel layers and the panels or discs which were to be tested. A weight of ~500 g was applied equally to each sample at 25 °C. Every 2 h, the discs of ethyl cellulose and plasticizer were removed from the fuel

layers and their weights were measured as precisely as possible. The difference between the recorded weights before and after each measurement was recorded as a function of NG migration. This procedure was repeated every 2 h for 10 h (Table 2).

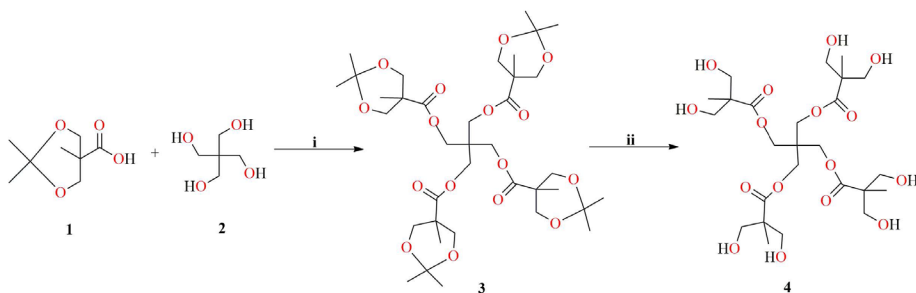
3.3.3 Preparation of the test samples for studying the migration rate by the FT-IR spectrum

To prepare the test samples, the synthesized polymer of poly(ϵ -caprolactone) (0.1 g) was dissolved in dichloromethane (10 mL) in a 25 mL flask equipped with a magnetic stirrer and *n*-BuNENA plasticizer (0.4 g) [synthesized according Ref. 20] was added. The reaction mixture was stirred at room temperature for 1 h and the solvent was then removed. The migration rate was studied using the FT-IR spectrum.

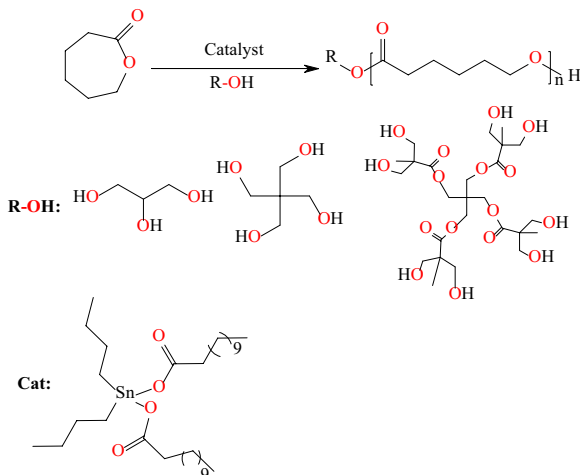
4 Results and Discussion

In order to investigate the NG migration, one should consider many different factors. The most important one in this regard is the homogeneity between the additive and the propellant matrix. On the other hand, the additive should not change the plasticizer's specific properties significantly. Of the additives usually used in propellants, ester and polyester plasticizers, such as poly(ϵ -caprolactone), should be useful for preventing NG migration.

Considering the migration mechanism, NG migration in an NC matrix can be attributed to two factors: (1) the electrostatic repulsion of the nitrate electron accepting groups ($-\text{NO}_3$) in NC and NG which leads to NG being expelled from the matrix towards the inhibitor, (2) the electrostatic attraction between the electron donating groups of the ester present in the inhibitor and the electron accepting nitrate groups present in NG, which cause the absorption of NG in the inhibitor. Based on the mechanism mentioned, it is clear that nitrate groups have a significant attraction to ester groups and can interact with them electrostatically [6]. The high NG absorption by a plasticizer may be explained on the basis of the structures of the plasticizer and nitroglycerine. The synthesis of a hyper branched initiator and plasticizers based on ϵ -caprolactone is shown in Schemes 1 and 2, respectively.



Scheme 1. Synthesis of hyperbranched initiator. (i) DPTS/DCC, 15 h, RT
(ii) Amberlite, MeOH, 3 h



Scheme 2. Synthesis of plasticizers based on ϵ -caprolactone

It is clear from the above structures that a polyester has several electron donor sites and NG has a number of electron acceptor sites. Thus, by addition of the plasticizer to the propellant formulation, an electrostatic force of attraction can act between them and reduce the migration/absorption of nitroglycerine from the propellant to the inhibitor. Thus, it may be supposed that the addition of the ester additive to the matrix is a suitable strategy for reducing NG migration. In fact, the ester groups can absorb nitrate groups existing in the NC matrix on the one hand, and can also absorb NG plasticizer on the other. As a result, they will significantly reduce migration.

Nitroglycerine absorption

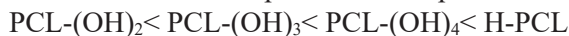
Nitroglycerine migration with samples containing 5 wt.% of the different synthesized plasticizers was studied (Table 2). It was observed that the sample containing the poly(ϵ -caprolactone) dendrimer plasticizer, had the highest ester attraction between plasticizer and nitroglycerine, and can act as the best one for reducing NG migration in propellants, in comparison with the other plasticizers. The nitroglycerine absorption data are shown in Table 2. The NG absorption of ethyl cellulose (EC) was 0.8 wt.% after 2 h and 6 wt.% after 10 h. NG absorption in poly(ϵ -caprolactone) diol (PCL-(OH)₂) was 8.2% after 10 h. This study indicated that NG absorption is further increased in the case of the hyperbranched poly(ϵ -caprolactone) (H-PCL). As we expected, the amount of NG absorption increased on going from PCL-(OH)₂ to H-PCL. On the other hand, NG migration can be decreased from propellants towards inhibitors. Therefore, according to Table 2, it was shown that dendrimer poly(ϵ -caprolactone) has the highest absorption level in comparison with the other plasticizers.

Table 2. Effect of time on nitroglycerine absorption by the plasticizers

Plasticizer \ Time	Nitroglycerine absorption [wt.%], time [h]				
	2	4	6	8	10
Ethyl cellulose ^a	0.8	2.5	4.3	5.1	6
PCL-(OH) ₂	3.3	5.2	6.3	6.7	8.2
PCL-(OH) ₃	3.5	5.7	6.8	8.1	10.5
PCL-(OH) ₄	3.7	5.6	7.2	8.9	11.2
H-PCL	4.2	5.9	7.3	8.7	12.3

^a Ethyl cellulose without plasticizer

The change in nitroglycerine absorption with time for PCL-(OH)₂, PCL-(OH)₃, PCL-(OH)₄ and H-PCL is displayed graphically in Figure 1. It is evident that the order of NG absorption can be represented as follows:



NG absorption depends on the number of polyester chains. Therefore, as the number of polyester chains increases, it is expected that NG absorption from PCL-(OH)₂ to H-PCL will also increase.

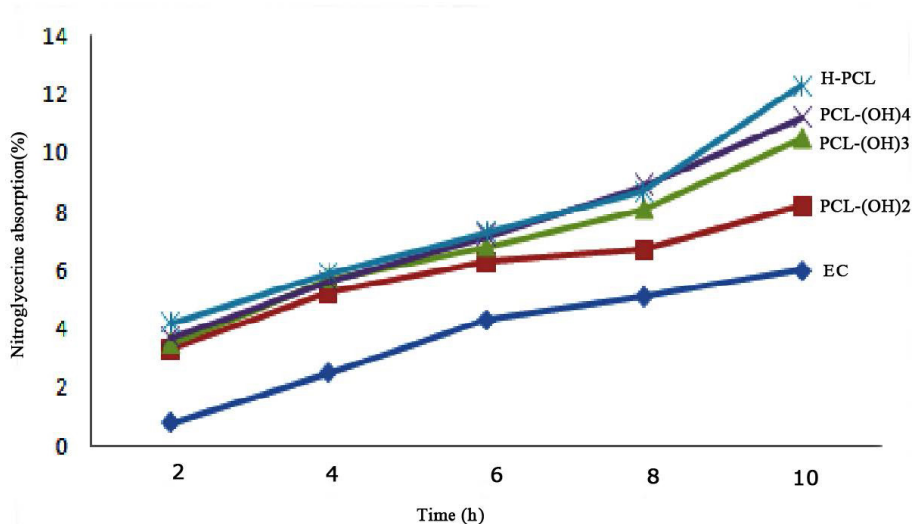


Figure 1. Effect of time on nitroglycerine absorption by the plasticizers

The results of observations of the interaction between the synthesized plasticizers of poly(ϵ -caprolactone) and *n*-BuNENA were also studied by means of FTIR spectroscopy. Because of the identical performance and lower sensitivity of *n*-BuNENA, it was used for investigating NG migration. Figure 3 shows the spectra of PCL-(OH)₂, *n*-BuNENA and a mixture of PCL-(OH)₂ and *n*-BuNENA. It is evident that spectral changes have occurred in the spectrum of PCL-(OH)₂ and *n*-BuNENA. The frequencies of C–H stretching vibrations in PCL-(OH)₂ (2945 cm⁻¹ and 2854 cm⁻¹) in the mixture containing PCL-(OH)₂ and *n*-BuNENA have changed. These bands had shifted to 2959 cm⁻¹ and 2874 cm⁻¹, respectively. The frequency of the C=O and C–O stretching vibrations of the ester groups had shifted from 1724 cm⁻¹ to 1728 cm⁻¹ and 1245 cm⁻¹ to 1267 cm⁻¹, respectively. The results of the study of the interactions between NG and the plasticizers synthesized in this work, showed the strongest hydrogen-bonding in the case of H-PCL.

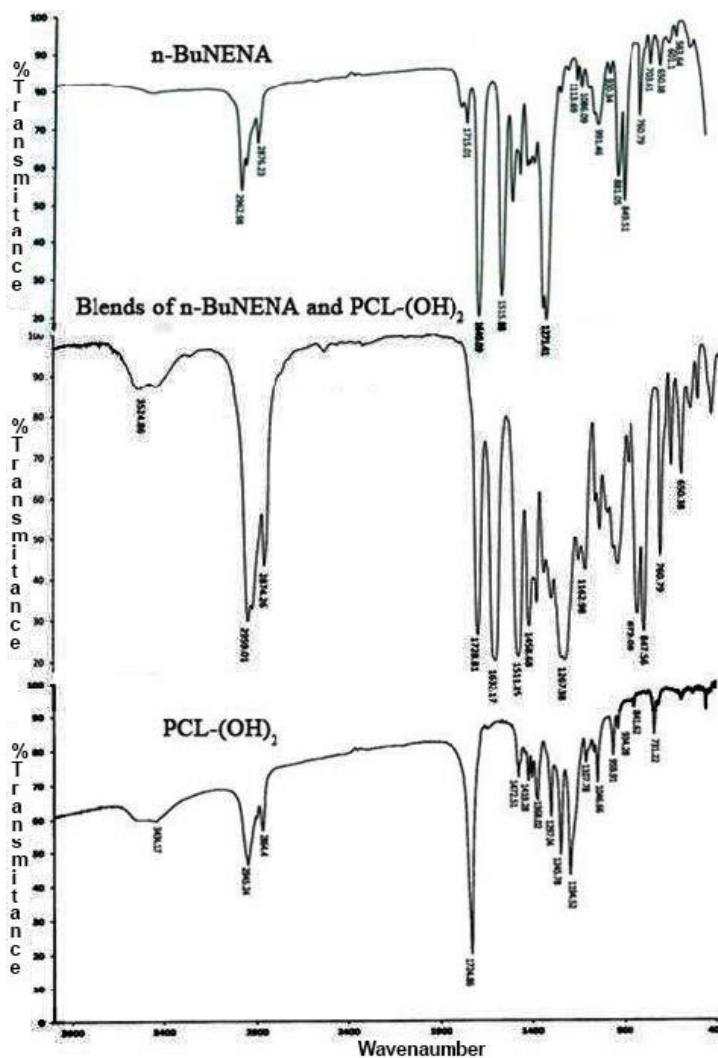


Figure 2. IR spectra of PCL-(OH)₂, *n*-BuNENA and a mixture of PCL-(OH)₂ and *n*-BuNENA

5 Conclusions

In this study, four green plasticizers based on poly(ϵ -caprolactone) were synthesized with a diol, a triol, a tetraol and a first generation dendrimer of the initiator. The Sandwich Test was used to investigate the migration of the

synthesized plasticizers. According to this study, when the number of electron donor sites is increased, NG absorption will be increased. On the other hand, NG migration can be decreased from propellants towards inhibitors. Also, by investigating the migration using the interaction between the synthesized poly(ϵ -caprolactone) and *n*-butylnitroxyethylnitramine (*n*-BuNENA) and observing changes in the FT-IR spectra, it was found that all of the synthesized plasticizers, with an attraction between electron acceptor groups of nitro in *n*-BuNENA and electron donor groups of the esters in the synthesized polymers, are effective in decreasing the extent of NG migration.

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