

Functional polymer from high molecular weight linear polyols and polyurethane-based crosslinking units: Synthesis, characterization, and boron retention properties

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ABSTRACT: The objective of this work was to synthesize functional polymers, with boron removal properties, from high molecular weight linear polyols based on *N*-methyl-D-glucamine (NMDG) and polyurethane units as crosslinking reagent. For that, (4-vinylbenzyl)-*N*-methyl-D-glucamine monomer (VbNMDG) was synthesized from vinylbenzyl chloride and NMDG, and subsequently, high molecular weight linear poly(VbNMDG) was obtained by radical free polymerization. Later, polymer dots were obtained from poly(VbNMDG) and urethanization reactions using methylene diphenyl diisocyanate at room temperature. Monomers and polymers were characterized by different techniques (FTIR, DLS, elemental analysis, ¹H-NMR). In addition, boron retention properties were studied by diafiltration technique using the azomethine-H method. It was concluded that synthesis of polymer dots, with high boron retention capacity, can be easily synthesized by procedure described. © 2016 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 43895.

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INTRODUCTION

Polyurethanes (PUs) are present in many applications of modern life. At present, coatings, adhesives, construction materials, synthetic fibers, paints, elastomers, and synthetic skins are produced from PUs in medical, automotive, and industrial applications.^{1,2} PUs can be defined as condensation polymers formed from polyisocyanates and polyols (monomers with at least two isocyanate units, —N=C=O and two hydroxyl groups, —OH). Some advantages of PUs are: (i) a high tensile strength and high melting points and, in consequence, these can be considered as durable materials; (ii) resistance to degradation by water, oils, and solvents make them excellent for the replacement of plastics; (iii) as coatings, PUs exhibit excellent adhesion properties to many substances, abrasion resistance, electrical properties, and weather resistance for industrial purposes; (iv) a high adaptability of their properties, that is, different properties can be produced by variations in the number of substitutions and the spacing of chains, structure can be designed to be linear to branched, flexible or rigid and, using low molecular mass polymers various block copolymers can be obtained with a high spectrum of tensile strength and elasticity.^{1–5}

Conversely, boron can be found in the nature in the form of boric acid, polyborates, or borate salt which is present commonly in seawater and minerals. Boron in form of boric acid is an essential micronutrient for the plants and its dosage or elimination of irrigation water is very important for different crops; in addition, water contamination by boron can come directly from industrial wastewater, agrarian products, and municipal sewage.^{6–9} Boron removal methods from aqueous solution are mainly adsorption, ion exchange, and membrane processes.⁹ Several polymeric resins have been developed to remove boron from water. Synthesis of adsorbent resins with selectivity to boric acid has been reported to be obtained from tris(hydroxymethyl) aminomethane, epoxy groups, and glycidyl methacrylate-divinylbenzene copolymer beads¹⁰; from 2-hydroxyethylamino propylene glycol prepared by the reaction of glycidyl with excess ethanolamine in *N*-methyl-2-pyrrolidone¹¹ and from poly(glycidyl methacrylate-*co*-trimethylolpropane trimethacrylate) functionalized with *N*-methyl-D-glucamine (NMDG).^{12–14}

Since PUs can be used as excellent structural materials, synthesis of functional PUs can be carried out for specific applications by the production of a material which can act simultaneously as support matrix and as functional material with capacity to interact with boron in aqueous solution. Different alternatives

can be developed by their combination with linear polyols, some options are: (i) interpenetrating polymer networks using PUs as primary network and polyols as secondary network, (ii) grafting polymers using PUs as main chain and polyols as grafting chains, and (iii) urethanization of high molecular weight polyols to improve their mechanical properties and extend their applications.

The objective of this work was to synthesize functional polymers, with boron removal properties from aqueous solution, from high molecular weight linear polyols based on NMDG and PUs units as crosslinking reagent.

EXPERIMENTAL

Reagents and Materials

Vinylbenzyl chloride (VbCl, Aldrich) and NMDG (Aldrich) were used in the synthesis of (4-vinylbenzyl)-*N*-methyl-D-glucamine (VbNMDG). Ammonium persulphate (Aldrich) was used as radical polymerization initiator. 1,4-dioxane (Aldrich) and bidistilled water were used as solvents. Methylene diphenyl diisocyanate (MDI, Aldrich) and poly(VbNMDG) were used as precursor of functional polymer. Cellulose membranes with different molecular weight cut-off, MWCO, were used for purification and fractionation of poly(VbNMDG) (Biomax PBGC, manufactured by Millipore Co.; MWCO: 1, 5, 10, 20, and 100 kDa). A stirred-cell filtration unit was used in experiment diafiltration (Millipore, model 8050); components and operation modes of the filtration system have been described by us in previous publications.^{15,16}

Functionalization of Vinyl Monomer

Dioxane and water, in 2:1 volume ratio, were placed in polymerization reactor and heated until total dissolution. Later, 3.20 mL (21.9 mmol) of VbCl was dissolved in 10 mL of dioxane and was slowly added to the reactor. The reaction was kept under reflux with constant stirring for 5 h. Unreacted VbCl was removed by extraction with ethyl ether and functionalized monomer (VbNMDG) remained in the aqueous phase.¹⁷

Characterization of VbNMDG was performed by crystallization. For that, a small fraction of aqueous phases was refrigerated and VbNMDG was crystallized, washed, and filtered with cold water. Later, monomer crystals were dried at room temperature for their characterization by nuclear magnetic resonance (¹H-NMR). The ¹H-NMR spectra were recorded on a Bruker Avance 400 spectrophotometer using dimethyl sulfoxide-*d*₆ (DMSO) as solvent and tetramethylsilane as internal standard.

Polymerization of VbNMDG

VbNMDG in aqueous phase was polymerized via free radical under nitrogen atmosphere, in refluxing conditions at 80 °C and constant stirring. Previously, 2.0% mol of ammonium persulphate with respect to initial monomer amount was added to the solution. After 24 h, reaction mixture was diluted to obtain a homogeneous solution. Polymer was purified by diafiltration using a membrane with MWCO of 1 kDa. Later, different fractions of molecular weights were obtained using membranes with MWCO of 5 kDa (1000–5000 g/mol), 10 kDa (5000–10,000 g/mol), 20 kDa (10,000–20,000 g/mol), and 100 kDa (20,000–100,000 g/mol for the permeate and molecular weight

larger than 100,000 g/mol for the retentate). Each fraction was analyzed to determine the reaction yield by elemental analysis and gravimetric analysis. In addition, polymer was characterized by FT-IR (Shimadzu, FTIR-8400), NMR for solid (Bruker Avance 400). Polymer fractions with major yields were analyzed by static light scattering (SLS) to determine their average molecular weight (M_w) using a Zetasizer Nano ZS90, model ZEN 3690. By this method, and applying the Rayleigh equation described by:

$$\frac{KC_{\text{pol}}}{R_{\theta}} = \left(2A_2C_{\text{pol}} + \frac{1}{M_w} \right) P(\theta) \quad (1)$$

where R_{θ} is the Rayleigh radius, A_2 is the second virial coefficient, C_{pol} is the polymer concentration, $P(\theta)$ is a function which describes the angular dependence of sample with the dispersed light, and K is the optic constant. Details of this method have been published.^{18,19}

Urethanization Reaction of High Molecular Weight Linear Polymer

Different molar ratio polyol:diisocyanate were used to carry out the urethanization reaction (1:0.25, 1:0.5, 1:1, 1:2, 1:3, and 1:5). Thus, 1.0 g of poly(VbNMDG) was dissolved in 4 mL of dioxane and MDI was added in the respective molar amount. Reaction was maintained at room temperature by one week to avoid the heating and thermal decomposition of polyol and MDI. Urethanization reaction was verified by FT-IR spectroscopy (Shimadzu, FTIR-8400) and by ¹³C-NMR using the CP-MAS technique and a Bruker^(R) 400 AC/PC (100 MHz).

Retention Experiments

Two types of retention experiments were performed: (1) boron retention capacity of poly(VbNMDG) and (2) boron retention capacity of functional polymers (i.e., product of reaction between poly(VbNMDG) and MDI).

Boron Retention Capacity of Poly(VbNMDG). Ten mL of 20 mmol/L poly(VbNMDG) solution was mixed with 10 mL of 20 mg/L boron solution. Different working pHs were used 5.0, 7.0, and 9.0; operating pressure and stirring rate were 300 kPa and 200 rpm, respectively. These operating conditions have been established in previous works.^{16,17} Permeate fractions with a volume of 20 mL were collected in plastic tubes to avoid interferences, and boron concentration was measured using azomethine-H method.¹⁷ A blank experiment was performed using the same experimental conditions but in absence of polymer. Boron retention (R_B) was calculated by

$$R_B = 1 - \frac{C_p}{C_0} F \quad (2)$$

where C_p is the boron concentration in the total permeate volume, C_0 is the initial boron concentration in the inside of ultrafiltration cell, and F is the filtration factor ($F = V_p/V_c$, where V_p and V_c are the permeate and retentate volume in the ultrafiltration cell, respectively.²⁰

Boron Retention Capacity by Batch-Type Experiments. Polymer samples were sieved by 425 μm to increase the contact surface. Later, 30 mg of polymer were contacted with 20 mL of boron

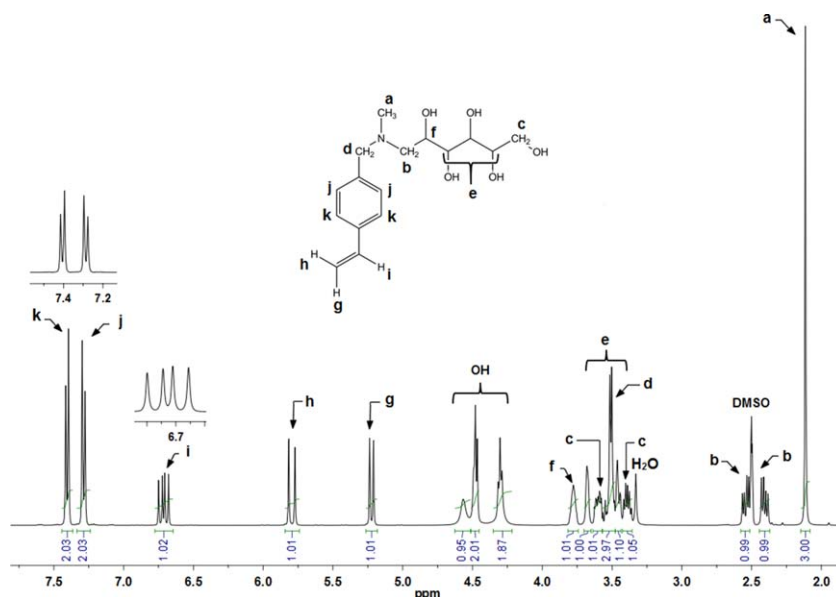


Figure 1. ^1H -NMR spectrum of VbNMDG. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

solution (20 mg/L) in the inside of ultrafiltration cell. After 24 h, ultrafiltration system was operated at the same conditions described in the Boron retention capacity of poly(VbNMDG) section. These experiment were performed for three molar ratio (1:1, 1:2, and 1:3 of poly(VbNMDG):MDI) at three pH values (5, 7, and 9).

RESULTS AND DISCUSSION

Synthesis of VbNMDG

VbNMDG was satisfactorily synthesized and purified by nucleophilic substitution of chlorine atom on VbCl by NMDG. Synthesis of VbNMDG was verified by NMR (see Figure 1). In the ^1H NMR spectrum, it can be seen a singlet at 2.11 ppm integrating for three protons corresponding to the methyl group (H-a). Two multiplets appear at 2.41 and 2.54 ppm, each one integrating for one proton, assigned to H-b. Likewise, two multiplets appear at 3.39 and 3.60 ppm and these integrate for one proton each one, assigned to H-c. Also, a singlet integrating for two protons corresponding to the protons H-d appears at 3.52 ppm. The multiplet that appears between 3.46 and 3.67 ppm integrating for three protons is assigned to the protons H-e and the multiplet at 3.78 ppm corresponds to H-f. The signals that appear between 4.30 and 4.57 ppm integrating for five protons are attributed to the protons in $-\text{OH}$ groups on the structure. Conversely, the doublet that integrate for one proton and appears at 5.23 ppm is assigned to the H-g ($J = 11.0$ Hz). Other doublet appears at 5.79 ppm integrating for one proton and is assigned to H-h ($J = 17.7$ Hz). A double doublet integrating for one proton appears at 6.74 ppm and is assigned to H-i ($J = 10.9, 17.7$ Hz). Finally, two doublets, each one integrating for two protons, corresponding to the protons of the benzene ring are observed at 7.29 ppm ($J = 8.1$ Hz) and 7.40 ppm ($J = 8.0$ Hz) and were assigned to H-i and H-k, respectively. It is important to note that no previous publications describing the isolation and characterization by NMR of VbNMDG.

Obtaining of High Molecular Weight Poly(VbNMDG)

Synthesis and Purification of Poly(VbNMDG). Later to synthesis of VbNMDG, the excess of VbCl was eliminated by solvent extraction; however, functionalized monomer was remained in the reaction aqueous phase. Thus, after polymerization reaction, poly(VbNMDG) was purified by variable volume diafiltration. It can be seen from Figure 2 that water soluble polymer purification can be satisfactorily carried out by this procedure. Decrease of UV absorption band of permeate samples is associated to the decrease of residual monomer and oligomers which can pass through the 1 kDa membrane (samples of permeates were denoted to be P1, P4, P7, and P9). In our case, nine fractions of permeate with a volume equal to volume initial in the UF cell were required.

Fractionation by Different MWCOs of Poly(VbNMDG)

Solution. Nitrogen percents (%N) measured for each polymer fraction and polymer percent obtained with different MWCO ranges are shown in the Table I. The largest amount of polymer

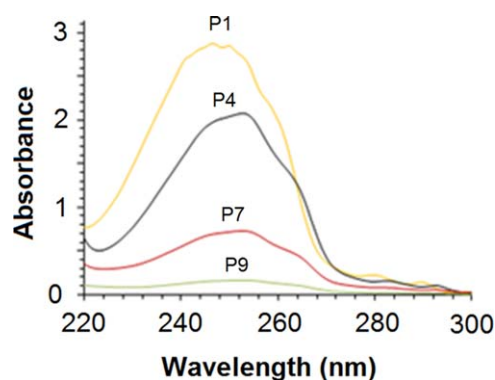


Figure 2. UV spectrum associate to the presence of residual monomer and oligomers in the permeate (P1, P4, P7, and P9 denote the permeate fractions 1, 4, 7, and 9, respectively). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Composition of Polymer Fractions Obtained by Diafiltration for Different MWCO

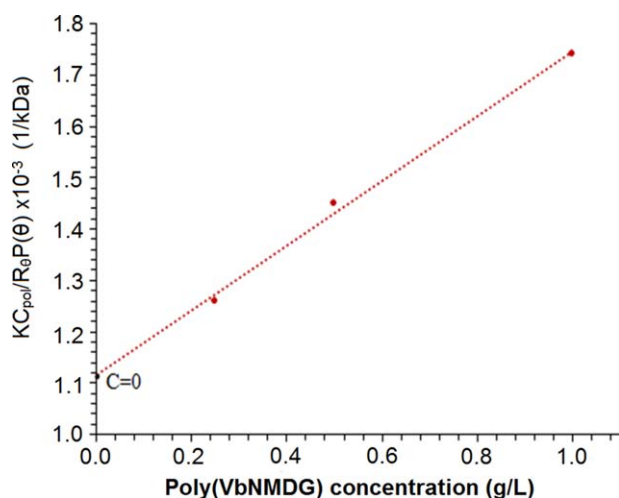
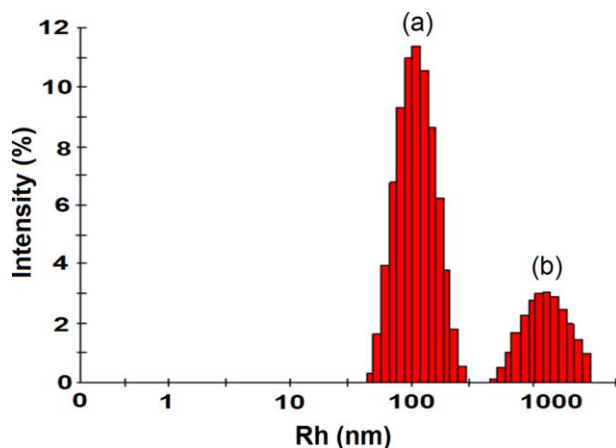
MWCO range	1-10 kDa	10-20 kDa	20-100 kDa	>10 kDa
% N	0.032	0.066	0.078	3.807
% poly(VbNMDG)	0.8	1.65	1.95	95.6

fraction was obtained for the retentate using a 100 kDa membrane (1.7421 g from 3.34 g of VbCl). By definition, MWCO suggests that 90% of polymer chains have a molecular weight larger than 100 kDa; therefore, it is expected that for this fraction only is present in solution high molecular weight polymer chains (in addition, polymer chains associated to 10% lower than 100 kDa were eliminated in the diafiltration using 5, 10, and 20 kDa membranes).

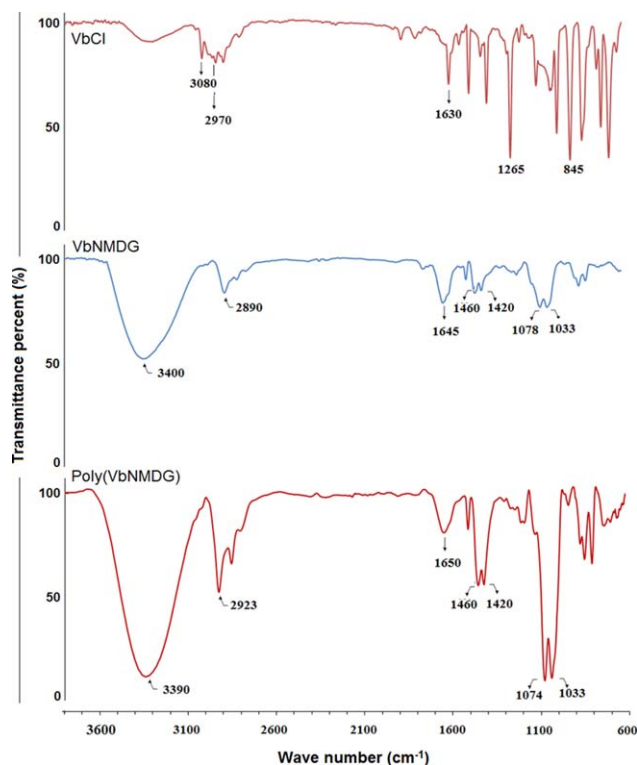
By static light scattering, average molecular weight obtained was 897 ± 22 kDa (i.e., on average, 2860 repeat units per polymer chains). Conversely, the value of second virial coefficient was 6.31×10^{-4} molmL/g², since this parameter is related with the interaction strength between polymer and solvent, it is suggested that particles in solution prefer to interact with solvent molecules than with other polymer chains. Experimental curve by static light scattering for the determination of M_w and A_2 are shown in the Figure 3.

Polydispersity obtained for poly(VbNMDG) with high molecular weight was 0.419 with a bimodal particle size distribution from hydrodynamic radius measures by light scattering. From Figure 4, two partial distributions can be identified; a first distribution between 40 and 300 nm with a mean value of 117.0 ± 42.7 nm and a second distribution between 500 and 3000 nm with a mean value of 1390 ± 564.3 nm.

Analysis of Poly(VbNMDG) by FT-IR. FT-IR spectra of poly(VbNMDG), VbCl and VbNMDG are shown in the Figure 5. By comparison of FT-IR spectra can be seen the disappearance

**Figure 3.** Experimental curve for the determination of M_w by static light scattering ($M_w = 897$ kDa, $A_2 = 6.31 \times 10^{-4}$ mol mL/g², $K = 7.22 \times 10^{-8}$ mol cm²/g at 24.9 °C). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]**Figure 4.** Particle size distribution from static light scattering: (a) 117.0 ± 42.7 nm and (b) 1390 ± 564.3 nm. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

of vibration bands at 845 cm⁻¹ and 1650 cm⁻¹ associated to the C—Cl and C=C bonds, respectively. Also, it can be appreciated vibration bands associated to C—O, C—N, and O—H vibrations at 1080 , 1033 , and 3400 cm⁻¹, respectively. Thus, by FT-IR was verified the monomer functionalization and polymerization reaction (because C—N and O—H vibrations only can be present in the polymer as a result of correct functionalization of VbCl with NMDG chains).

**Figure 5.** FT-IR spectra of VbCl, VbNMDG, and poly(VbNMDG). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

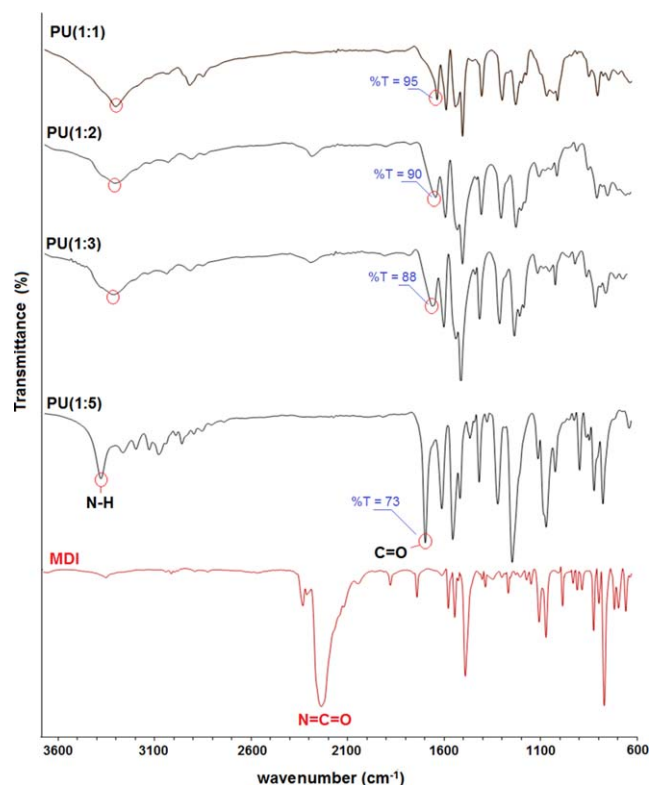


Figure 6. FT-IR spectra of polyurethanes, PU, at different MDI:polyol ratio (1:1, 1:2, 1:3, 1:5). PU_{EIG} (1:5) corresponds to polyurethane synthesized from MDI and ethylene glycol with 1:5 ratio. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization of Functional Polymers from MDI and Poly(VbNMDG) by FT-IR. Functional polymer FT-IR spectra are shown in the Figure 6. Main evidences of the formation of urethane groups are: the appearance of absorption band around $1700\text{--}1650\text{ cm}^{-1}$, which corresponds to —C=O bond and the disappearance of the bands around $2250\text{--}2200\text{ cm}^{-1}$ corresponding to vibration of —N=C=O . In addition, it can be identified the wide absorption band associated to hydroxyl groups of polyol at 3400 cm^{-1} .

The increase of absorption band intensity associated to C=O bond, with the increase of poly(VbNMDG) amount, suggests

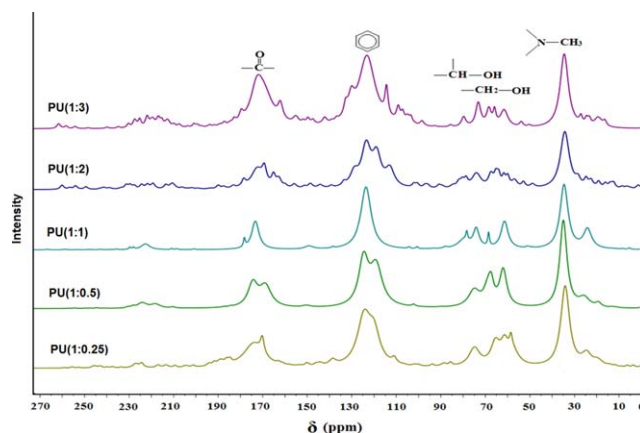


Figure 7. ^{13}C -NMR spectra of polyurethanes based in MDI and poly(VbNMDG). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

that a major amount of urethane groups were formed [in the Figure 6, percentage of transmittance change from 95 to 73 for PU (1:1) and PU (1:5), respectively]. Conversely, with the decrease of poly(VbNMDG) amount, more intense absorption bands associated to —OH groups can be identified suggesting that more hydroxyl groups are available for desired application (i.e., boron retention). By comparison between functional polymer with poly(VbNMDG) can be clearly identified the absorption band associated to N—H bond; its high relative intensity can be explained by a major amount of VbNMDG units, however, it is suggested that a minor number of hydroxyl groups is available to interact with boron for retention application. The incorporation of VbNMDG units was verified by nitrogen percent (%N) determined by elemental analysis (see Table II).

Characterization of Functional Polymers from MDI and Poly(VbNMDG) by ^{13}C -NMR. Chemical displacement for some characteristic signs as aromatic, aliphatic, and carbonyl group signs were identified by solid ^{13}C -NMR of polyurethanes (see Figure 7). Between $\delta 30$ and 35 ppm a sign corresponding to carbons of CH_3 , which are linked to the nitrogen of VbNMDG can be identified. Signals around $\delta 60\text{--}75\text{ ppm}$ are

Table II. Comparison of %N Measured in the Polyurethane Samples and Calculated from Amount Added to the Mixture Reaction; and VbNMDG Units which was Incorporated to the Polyurethane Matrixes

Sample	% N (Expected)			% N	[VbNMDG] ^a
	Poly(Vb-NMDG)	MDI	PU		
Poly(Vb-NMDG)	4.498	0.000	0.000	3.807	2.72
R 1:0.25	3.749	1.865	5.614	5.408	2.67
R 1:1	2.499	4.981	7.480	7.529	1.78
R 1:2	1.728	6.893	8.621	8.097	1.23
R 1:3	1.319	7.909	9.228	8.557	0.94
R 1:5	0.896	8.953	9.849	9.051	0.64

^a [VbNMDG]: Amount expressed in mmol of VbNMDG/g of resin.

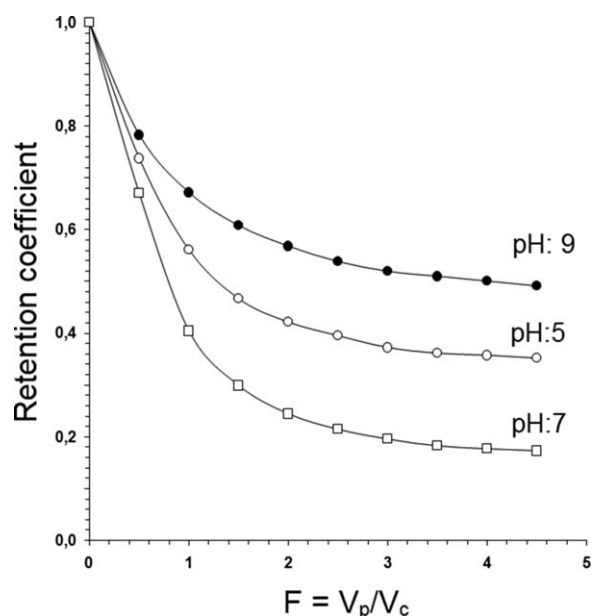


Figure 8. Retention profiles for poly(VbNMDG) for different pH values (5, 7, and 9).

mainly assigned to carbons linked to the hydroxyl groups. Signals between $\delta 120$ – 130 ppm and $\delta 165$ – 175 ppm are assigned to aromatic and urethane carbons, respectively.

Boron Retention Properties of Poly(VbNMDG) and PUs

Although synthesis of PUs using poly(VbNMDG) and MDI was satisfactory, PUs using 1:0.25, 1:0.5, and 1:5 ratios of polyol:diisocyanate were not obtained with high yields. In consequence, retention experiments were performed only with three polyol:diisocyanate ratios (1:1, 1:2, and 1:3).

Binding mechanism of boron by NMDG chains has been described by different authors.²¹ Boron retention by poly(VbNMDG) and PUs can be explained by the presence of available NMDG chains. Thus, NMDG groups capture boron through a covalent attachment and formation of an internal coordination complex between two hydroxyl groups in position *cis*. Retention profiles for each pH are shown in the Figure 8 and milligrams of retained boron per mass of PU are shown in the Figure 9.

For poly(VbNMDG), boron retention capacity showed the following order: pH 9 > pH 5 > pH 7. Thus, mol of boron per mol of poly(VbNMDG) were 0.78, 0.039, and 0.45 for pHs 9, 7, and 5, respectively. Effect of pH on retention properties is directly related with properties of Boric acid. Boric acid is a very weak acid with a pK_a value of 9.2. At a lower pH than 7, boron is present in its nondissociated form (boric acid) and at a pH greater than 10.5, it is present in the dissociated borate form. For pH > 9.2 the borate monovalent anion $B(OH)_4^-$ is formed and retention is decreased, for pH < 7.0, tertiary amine on NMDG is protonated and polymer structure is positively charged. In studies of boron removal by water soluble polymers based in NMDG groups,^{14,22,23} high values of boron retention were obtained at a basic medium being the boron retention enhanced by the increase in pH (retention values near to 80%).

In our case, relatively low boron retentions were obtained. These results are congruent with reported by Yurum *et al.* (2013) using NMDG-grafted polyglycidylmethacrylate and obtaining a boron retention of 51.4% at pH 9.0 (in this study $R_B = 50$ at pH 9.0).⁷ However, as retention coefficient is a relative value, comparison of results for different concentrations in the feed are not adequate from studies previously published under different experimental conditions. In addition, an effect of boron concentration in the feed, boric acid speciation, membrane nature, filtration process (e.g., ultrafiltration or reverse osmosis) and protonation of amine groups on boron retention have been reported with different results.^{14,22,23} However, it is evident for us that more detailed studies in relation with the effect of some parameter of retention and on standardization of polymer-enhanced ultrafiltration technique for the study of retention properties of water soluble polymers are required (i.e., unification of experiment design and result report).

Conversely, for PUs, it can be seen that as amount of MDI was increased a decrease of boron retention was observed; thus, for a low amount of MDI is major the number of available glucamine chains to interact with boron in solution. In addition, an effect of pH on boron retention was not evidenced when polymer-diisocyanate ratio was 1:2 whereas for 1:1 ratio the boron retention presented the same behavior observed for linear poly(VbNMDG) in aqueous phase.

Results suggest that there is an important effect of poly(-VbNMDG):MDI ratio on boron retention properties of functional polymer synthesized. This can be explained by the linking point in the formation between urethane groups. Thus, for high relative amount of MDI the probability of the formation of urethane groups with adjacent hydroxyl groups is increased and, in consequence, the number of hydroxyl groups in placement *cis* for the formation of tetraborate complex is decreased affecting the retention value. Conversely, for low relative amount of MDI, the number of available NMDG chains is large and therefore their interaction with boric acid in solution is favored and very similar to interaction expected for linear poly(VbNMDG).

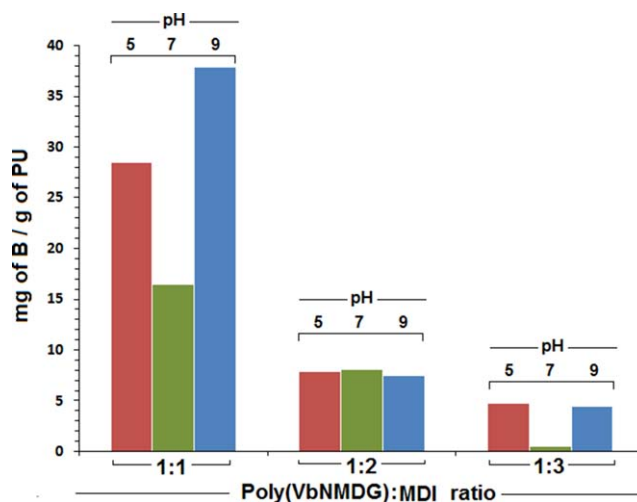


Figure 9. Retention of polyurethane synthesized at different poly(VbNMDG):MDI ratios at different pH (5, 7, and 9). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

In all cases, physical appearance of these polymers was like polymer dots easily dispersible in water; in addition, these functional polymers can be easily retained by filtration suggesting that can be enclosed in open systems with small pore size. Previous features permits that polymers can be used in column systems.

CONCLUSIONS

Functional polymers synthesized from poly(VbNMDG) and MDI can be synthesized from procedure described in this study. Vinyl monomer precursor for free-radical polymerization can be synthesized from VbCl and VbNMDG, purified by solvent extraction and isolated by crystallization for its correct characterization according to procedure described by us. Synthesis of high molecular weight poly(VbNMDG) can be performed from VbNMDG in aqueous phases (water-dioxane phase) posterior to the extraction procedure of residual VbCl. In addition, fractionation by diafiltration of polymer reaction mixture was found to be efficient and can be limited to the use of 100 kDa membrane. Synthesis of functional polymers can be performed at low temperature but, for boron retention application, it was seen that low poly(VbNMDG):MDI ratio are more adequate. Boron retention capacity of poly(VbNMDG) was similar to that observed for PU prepared from relative high poly(VbNMDG) amounts (effect of pH in this case was: $\text{pH } 9 > \text{pH } 5 > \text{pH } 7$). Finally, it is concluded that synthesized functional polymers are a potential alternative to develop systems of boron retention from aqueous solution.

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