





RESEARCH ARTICLE

Polyurethanes synthesized with polyols of distinct molar masses: Use of the artificial neural network for prediction of degree of polymerization

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Abstract

The molar mass of the polyurethanes (PUs) reagents directly influences their thermal response, affecting both the polymerization process and the enthalpy and the degree of reaction. This study reports applying an artificial neural network (ANN), associated with surface response methodology (SRM) models, to predict the calorimetric behavior of certain PU's bulk polymerizations. A non-catalyzed reaction between an aliphatic hexamethylene diisocyanate (HDI) and a polycarbonate diol (PCD) with distinct molar masses (500, 1000, and 2000 g/mol) was proposed. A high level of reliability of the predicted calorimetric curves was obtained due to an excellent agreement between theoretical and modeled results, enabling creating a 3D surface response to predict the reaction kinetics. Also, it was possible to observe that the polymerization kinetics is affected by the —OH group's association phenomena. The applied methodology can be extended for other materials or properties of interest.

KEYWORDS

artificial neural network, differential calorimetric analysis, molar mass, polyurethane

1 | INTRODUCTION

Polymerization plays a significant role in industry and academia because tailor-made properties can be obtained by a profound understanding of the relationship between reagents' reactivity and structure. Polycarbonate-based

polyurethanes (PUs), for example, are standing out in the biomedical area due to their lower susceptibility to hydrolysis compared to polyester-based PU and oxidation compared to polyether-based PU, besides excellent mechanical properties, controlled degradation, and biocompatibility.^[1-4] These polymers are formed by a

sequence of parallel step-growth polymerization reactions that allow, at least in principle, to predict the system's specific composition with time accurately. As a result, a polymer with a two-segment structure is formed. The thermodynamic incompatibility between soft and hard segments of PUs leads to a microphase separation, revealed in a rubber-like matrix containing hard microdomains.^[5] The flexible phase is a polyol, which implements the rubber-like characteristic and elasticity of the elastomers. The reaction of a polyol with diisocyanate generates the polymers' rigid phase. The isocyanate is highly reactive and creates products chemically different when combined with active hydrogen ($-OH$ and $-NH$ functional substances), forming urethane and urea groups. Chain extenders (e.g., short-chain diols and diamines) are used as additives in the production of PUs to increase the molar mass of polymer and improve their properties.^[6-8] Therefore, the suitable variation in the oligomers' structure and chemical composition allows to produce tailor-made materials, broadening the range of PUs applications, including packaging, cables, textile coatings, medical implants, biodegradable adhesives, foams, among others.^[9-11]

An increase in the soft segment chain length usually increases the crystallinity degree and the microphase separation, thus enhancing the rubber-like mechanical properties and thermal stability.^[12] The reaction kinetics can be affected by chain length, reactivity/content of the reagents, and chemical groups, which interfere in the soft and hard building blocks' dynamics. The quantitative perception of the polymerization kinetics is essential to assess polyurethane industrial design and directly influence the type of morphology formed in the copolymer, as well as the physical and mechanical properties.^[2,13,14] Several characterization methods have been used to measure the kinetics of polymerization reactions. The approaches fall into two groups: (i) indirect techniques that measure a physical property functionally related to the reaction extent and (ii) direct methods that measure a reagent or product concentration. Among the indirect thermal methods used to control the kinetics' polymerization reaction, differential scanning calorimetry (DSC) is the most used for accompanying the curing process.^[2]

Traditionally, the selection of proper theoretical kinetic models can adequately describe the experimental data. Nevertheless, the models rarely give a precise representation of all aspects present in the experiments because they can only represent the reaction's chemical nature. Other factors as specimen geometry, thermomechanical history, volatility, and so on can also influence the results. These conditions inflict several experimental design problems in data analysis and interpretation of results.^[15] In this context, artificial neural

networks (ANNs) and quantitative structure–property/activity relations (QSPR/QSAR) approaches have been widely studied due to the results' reliability.^[13,16,17] Unlike QSPR/QSAR, quantitative structure–property/activity relations), which followed a mathematical rule to calculate a specific property (such as reaction enthalpy) from descriptors attributes (topological, structural or conformational), ANN systems operate based on comprehensive statistical curves.^[18-21] Maybe the QSPR/QSAR model's main drawback is that the analyses lack design in the strict sense of experimental study. The analyzed data collected may not reproduce the whole attribute space. Consequently, several QSAR results cannot predict the probable composites with the most suitable activity safely. In this context, the ANN is an interesting and powerful mathematical tool that enables the optimization and prediction of data based on the input information without any physical model assumptions. However, because they do not require any knowledge about the data source, ANNs use the estimation of many weights that requires large training sets, which may be the most significant drawback of this method. The combination of QSPR/QSAR with ANN has also been studied by other authors.^[22] Considering that different parameter combinations can significantly increase the experimental number and analysis time, Box and Wilson^[23] tested the surface response methodology (SRM) tool to obtain an optimal response in the experiments' design. SRM reduces the number of experiments to obtain results not performed experimentally, keeping statistical relevance and when combined with ANN can significantly improve the results' reliability.^[23-25]

Therefore, this study aims to apply the ANN approach to fit the DSC curves of PUs produced from a polyol with different molar masses at four different heating rates. The ANN simulated curves were used to create a 3D surface plot (by SRM), allowing to predict any DSC curve situated inside the range studied. Consequently, the prediction of the polymerization degree concerning the PUs molar mass is also possible. We believe that this work will reduce a large number of experimental data for the characterization of materials. This new data processing methodology can be expanded to predict the polymers' enthalpy reaction and other properties of interest, reducing cost and analysis time.

2 | MATERIALS AND METHODS

2.1 | Materials

The polyols Eternacoll PH50 (hydroxyl number 224 mg KOH/g, molecular weight 500 g/mol, functionality of 2,

viscosity at 75°C = 65–120 cP), PH100 (hydroxyl number 110 mg KOH/g, molecular weight 1000 g/mol, functionality of 2, viscosity at 75°C = 400–630 cP, density 1.22 g/cm³) and PH200 (hydroxyl number 56 mg KOH/g, molecular weight 2000 g/mol, functionality of 2, viscosity at 75°C = 2200–2800 cP) based on a mix of 1,5-pentanediol and 1,6-hexanediol, were used as polycarbonate diol (PCD) and furnished by UBE Corporation Europe (Spain). This monomer was dried at 80°C under vacuum for 6 h before use. The isocyanate 1,6-hexamethylene diisocyanate (HDI, 99 + % purity, CAS number: 822-06-0) with the functionality of 2 and a free isocyanate index of 49.72 ± 0.07 wt.% (determined by *n*-dibutylamine titration according to the ASTM D-2572) was provided by Vencorex Chemicals (France) and used as-received.

2.2 | Synthesis and monitoring of the polymerization reaction

The PUs were synthesized without the use of organic solvents and at stoichiometric amounts (1.0 NCO/OH molar ratio) of 1,6-hexamethylene diisocyanate (HDI) and polycarbonate diol (PCD). The three polyols aforementioned produced PUs with *M_w* of 500 (PU500), 1000 (PU1000), and 2000 (PU2000) g/mol. These reagents were manually mixed for 5 min at room temperature and transferred on aluminum crucibles for DSC analysis. No catalyst was employed for avoiding biocompatibility problems of the material in applications aimed at tissue engineering.

The polymerization reaction of the samples was monitored via DSC-50 Shimadzu equipment in the following conditions: c.a. 10 mg of sample, N₂ atmosphere (50 ml/min), and heating range from 25 to 180°C at 5, 10, 15, and 20°C/min for all samples. The *M_w* of the PUs was determined by size exclusion chromatography (Perkin Elmer series 200 chromatography) under the following conditions: dimethylformamide with 1% of LiBr (eluent), 10 mg/ml sample's concentration, 1 ml/min flow rate, 10 µl injected volume, columns temperature of 35°C, and polystyrene (PS) standards for the calibration curve.

2.3 | Artificial neural network and surface response methodology

The ANN curves were fitted using the DSC experimental data of the samples at the four heating rates. The following fit conditions were used: 1 layer with 12 hidden layers, 5 training repetitions, resilient backpropagation with backtracking as the algorithm, and the sum of

squared errors as the error function (threshold of error function 0.1). The activation function used was the rectified linear unit (ReLU). All the ANN fitted curves were used for SRM. Equation (1) describes the SRM approach used; *Y* represents the predicted response, *x_i* and *x_j* are parameter variations (*x*- and *y*-axis), β₀ is the constant coefficient, β_{*i*} is the linear coefficient, and β_{*ij*} is the interaction coefficient. More details about these methods can be found in the literature.^[13,17,26]

$$Y = \beta_0 + \sum_{i=1}^k \beta_i x_i + \sum_{i=1}^k \beta_{ii} x_i^2 + \sum_{j=1}^k \beta_j x_j + \sum_{j=1}^k \beta_{jj} x_j^2 + \sum_{i=1}^{k-1} \sum_{j=i}^k \beta_{ij} x_i x_j \quad (1)$$

2.4 | Predicting the degree of polymerization

The nonisothermal curves at the four different heating rates based on the ANN dataset were used to simulate the degree of polyurethane reaction. The curves were processed with *Netzsch Thermokinetics, a Software Module for the Kinetic Analysis of Thermal Measurements*.^[27] The dependence between activation energy (*E_{a(T)}*) on the conversion degree (*α_(T)*) was assessed by the isoconversional methods of Flynn–Wall–Ozawa (FWO),^[28] Friedman (FR),^[29] and Kissinger–Akahira–Sunose (KAS).^[30] A “Multivariate Non-linear Regression” program evaluated the corresponding kinetic parameters using a hybrid Marquardt–Levenberg approach. All theoretical curves are simultaneously compared with experimental ones by using the F-test method. By using the least-square method, the proper model is selected (using the F critical value). The model proposed by Prout–Tompkins (*B_{na}* mechanism) was elected for representing the polymerization mechanism and to present the best fit. The selection has a physical meaning since the synthesis of urethane compounds depends on an isocyanate and alcohol chemical groups' equilibrium with an autocatalytic nature (as previewed by the model). The simulated curves were used to predict the isothermal polymerization behavior. The conversion degree (*α*) during the polymerization has been calculated with Equation (2):

$$\alpha_{\text{DSC}} = \frac{\Delta H_T}{\Delta H_{\text{dyn}}} \quad (2)$$

where Δ*H_T* is the heat released up to a temperature *T* (obtained by integrating the calorimetric signal in this

temperature range), and ΔH_{dyn} is the total reaction heat correlated with the full conversion of all reactive groups. The α parameter was estimated as the mean value for heat reaction attained dynamically at the various heating rates.

3 | RESULTS AND DISCUSSION

The molar masses (M_w) of the materials obtained after polymerization were 152,150, 178,251 and, 165,022 g/mol for PU500, PU1000, and PU2000, respectively. The polydispersity index (M_w/M_n) for all samples was ~ 1.59 without gel formation for the PUs. On stoichiometric amounts of isocyanate and $-\text{OH}$ groups, higher molar mass PUs was obtained.^[2] The autocatalysis phenomenon occurs when the products catalyze the reaction. The reaction progress for the samples was determined through DSC analysis by measuring the exothermic peaks in the heat flow rate curves. The DSC curves of the PUs with different molar masses are presented in Figure 1.

This polymerization process is quite slow compared to different polyurethane systems, such as those comprising aromatic diisocyanates, which can be explained by considering thermodynamics aspects and the difference in reactivity between aliphatic or aromatic chain isocyanates.^[2,6,31] Besides the thermodynamic factor, the hard segment's mobility and interactions and the system's viscosity also control the phase structure formation.

The ANN modeling for the PU1000 thermal results at distinct heating rates is shown in Figure 2. Since the other samples (PU500 and PU2000) displayed very similar behavior, the fits are not illustrated. The symbol dots represent the experimental results, while the solid lines are the fits derived from the ANN mathematical approach. As a first approximation, the results are

satisfactory, mainly for a practical application of polymer properties. Despite a not perfect fit, the fitted peak practically coincides with maximum experimental temperature, which means that for some kinetic models that consider the maximum reaction (e.g., Kissinger), the present fit would already be satisfactory.

In Figure 3(A), the regression plot shows an excellent fit. It means that the model presented a successful effect of adding another variable to a model that already has one or more independent values. In the residual plot (Figure 3(D)), the residuals and the independent variable are represented in the vertical and horizontal axes, respectively. Since the residual results are randomly scattered along the horizontal axis, a linear regression model becomes suitable for treating the data. Finally, cross-validation proved that statistical analysis results would be generalized to an independent data set. This is indicative of how precisely a predictive model will operate in practice.

We also recognized from a three-dimensional plane that DSC behavior is predicted both by heating rate and molar mass variation. Nonetheless, a well-trained ANN contributes to developing a mechanistic understanding of the material examined, considering it as a phenomenological approach. Figure 4 exhibits the SRM results from the predicted ANN database, considering temperature (x-axis) and heating rate (y-axis) parameters variation. It is also possible to predict the thermal behavior curve from different heating rates, not applied experimentally, but with a high-reliability level.

An increase in the peak heating flow (z-axis) with the heating rate is observed for all samples. On the other hand, the heating flow area (z-axis) tends to decrease for PU1000 (Figure 4(B)) and PU2000 (Figure 4(B)) with exception of PU500, which increases the heat flow. This behavior probably occurs due to the increase in the molar mass and viscosity, which difficult a uniform distribution

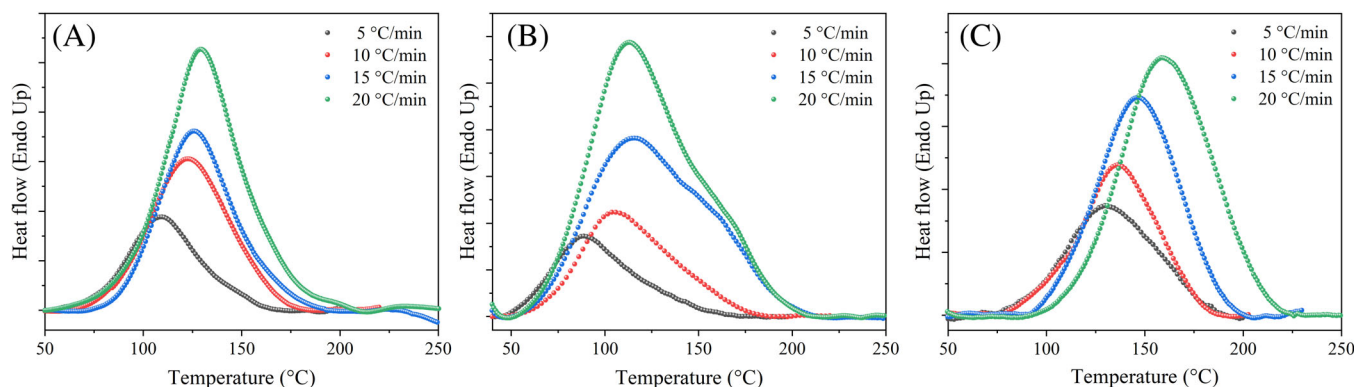


FIGURE 1 Differential scanning calorimetry (DSC) curves at different heating rates of polyurethane (PU) samples synthesized from a polyol of different molar masses (A) PU500, (B) PU1000, and (C) PU2000 [Color figure can be viewed at wileyonlinelibrary.com]

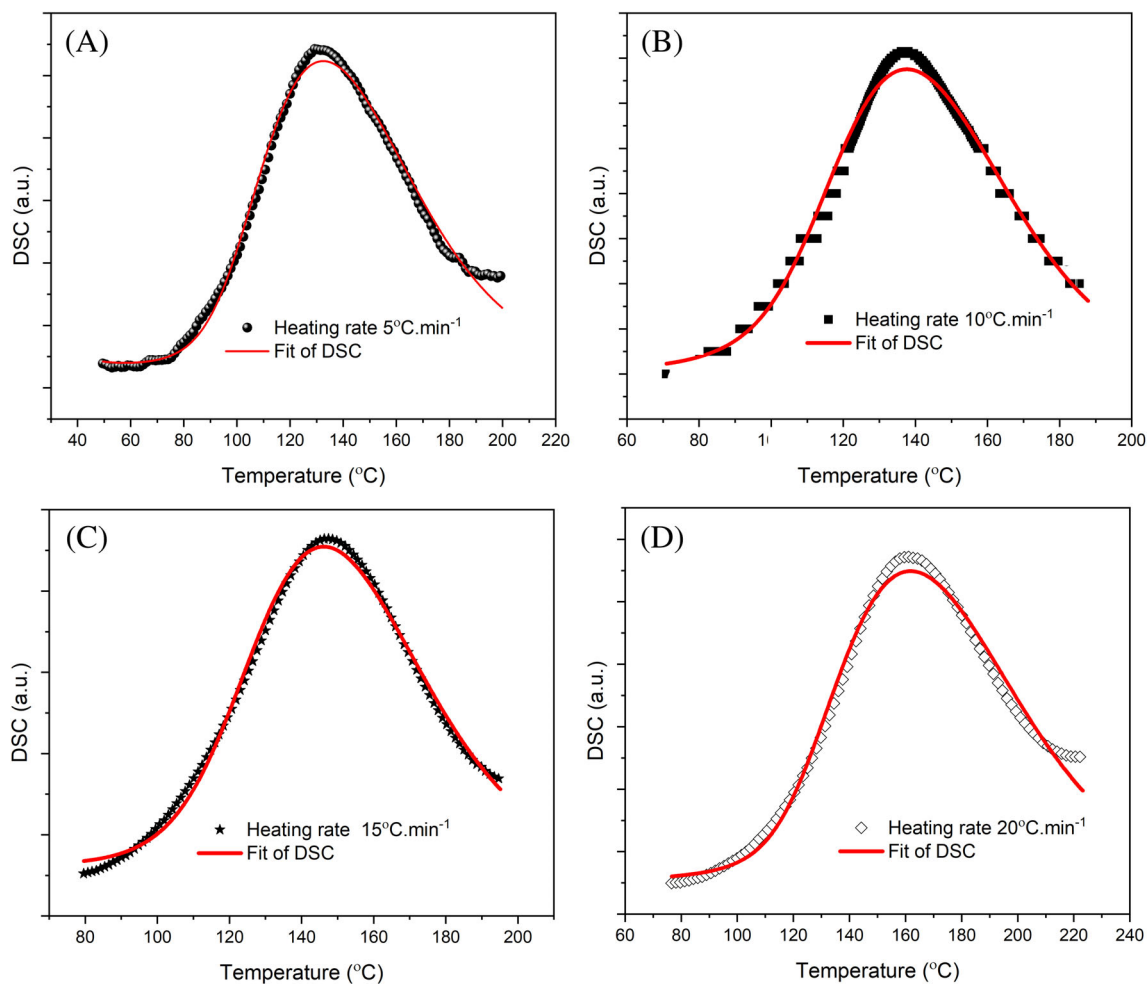


FIGURE 2 Artificial neural network (ANN) fitting for the PU1000 thermal curves at the four different heating rates [Color figure can be viewed at wileyonlinelibrary.com]

of heat along the chains. This event is properly reported in the bulk polymerization of PUs.^[14,32] Also, the association phenomena within $-\text{OH}$ groups by intramolecular and intermolecular hydrogen interactions have a well-known effect, which certainly influences the reactivity of such groups toward isocyanate functions.^[14,33] In stoichiometric circumstances, the association phenomena can proportionally occur for both conditions: with a decrease of the macrodiol's molar mass or as a consequence of the intramolecular hydrogen interactions.

The difference in the polymerization behavior is seen in Figure 5, which shows the SRM results based on the ANN data. The heating flow curves (z-axis) were predicted based on temperature (x-axis) and molar mass variation (y-axis) using Equation (1). The curves presented were simulated for $10^\circ\text{C}/\text{min}$ (Figure 5(A)) and $20^\circ\text{C}/\text{min}$ (Figure 5(B)) heating rates, but they can be simulated for any other heating rate. For both heating rates, the range variation of heating flow is more significant for PU500, as mentioned earlier. There is a trend in

the peak displacement at higher temperatures for higher molar masses, probably due to the direct relationship between the peak reaction and the polyol molar mass. Combining the ANN data set with the SRM model is created the possibility of predicting heating flow curves for different polyol molar mass values.

The heating flow curves simulated by combining the ANN data set with the SRM model were used to calculate the three PU's degree of reaction (Figure 6(A)). It is possible to observe that the PU500 initiates the polymerization at lower temperatures than the other samples. The values obtained for the PU reaction kinetics are shown in Table 1. The B_{na} model (used for describing the autocatalyzed reactions) exhibited a strong correlation (close to unity), and similar $E_{\alpha(T)}$ values compared to the kinetic models used (FR, FWO, and KAS models). Considering the overlapping between the data, it can be related that the combination of the ANN and SRM, considering the autocatalytic model as the reaction mechanism, adequately represents the polymerization kinetics of PU (Figure 6(B)).

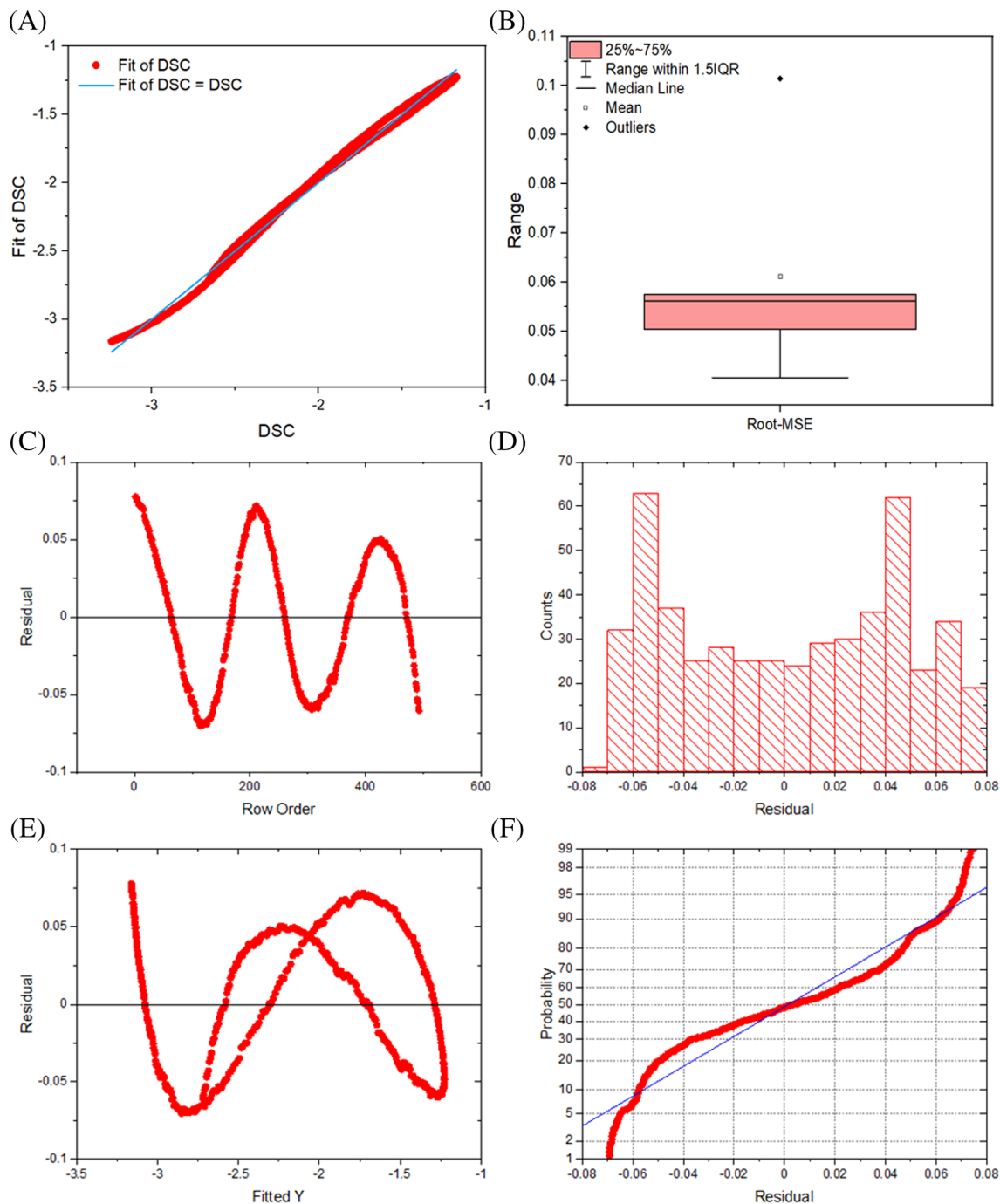


FIGURE 3 (A) Regression plot for PU1000 at 15°C/min, (B) cross-validation root-MSE box plot, and (C–F) residual plot [Color figure can be viewed at wileyonlinelibrary.com]

As shown in Table 1, the $E_{\alpha(T)}$ remained practically constant for PU500 and PU1000. Lower $E_{\alpha(T)}$ values were obtained for PU2000. Eceiza et al.^[14] also obtained comparable rate constants for PUs with 775 and 1015 g/mol, produced from polycarbonate diols and 4,4'-diphenylmethane diisocyanate at the same temperature. These samples had a rate constant lower than a sample with 1990 g/mol, confirming that the —OH group's association phenomena depend on the diol's molar mass and chemical structure.

Furthermore, these phenomena were more expressive for polycarbonate diols with lower molar mass or higher —OH group concentration and higher significance for polycarbonate diols with —OH groups in chain ends of an odd number of carbons atoms. The activation energy decrease by the increase of the association phenomena. A corresponding trend has been noted for the activation energies obtained in the reaction between PCD and HDI.^[2] This suggests that the association phenomena can

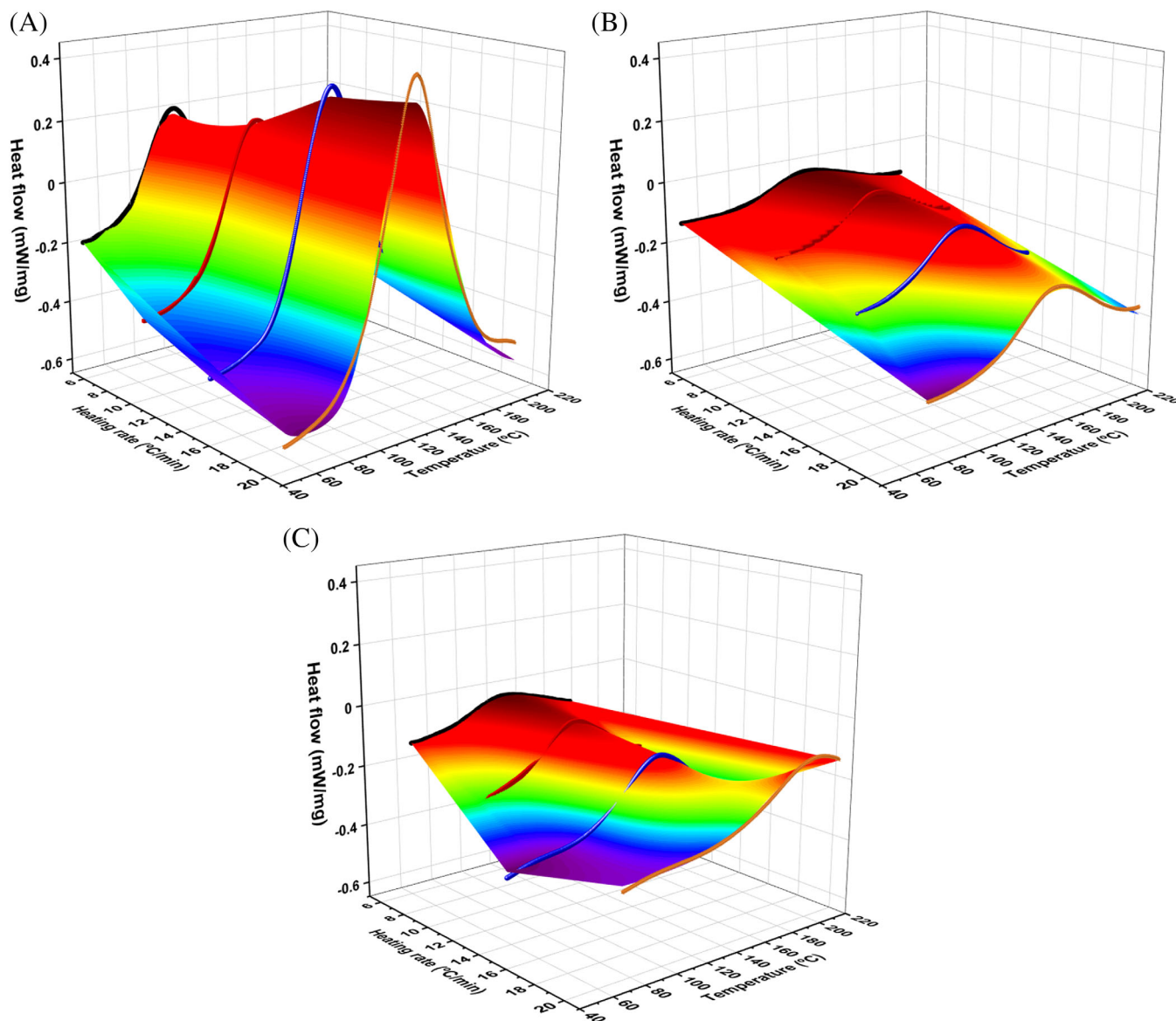


FIGURE 4 Surface response methodology (SRM) curve based on artificial neural network (ANN) dataset: (A) PU500, (B) PU1000, and (C) PU2000 [Color figure can be viewed at wileyonlinelibrary.com]

improve —OH groups' nucleophilicity by forming a reaction complex with —NCO groups or by reacting with the complex itself, as reported in mechanisms catalyzed by alcohol and urethane.^[34]

Also, both molar mass and viscosity increase continuously as such reactions proceed. The polymer molecules may become insoluble above a critical chain length or molar mass. The low molar mass byproducts would gradually accumulate in the system, inducing equilibrium to shift toward the reactants. All these factors may influence the polymerization rate considerably.^[32] The rate at which independent functional groups react for chain extending from new condensed interunit linkages depends on three distinct processes: one in which the groups diffuse into a cage, another in which the groups spread separately, and a

third, in which the groups trapped in the cage react to form a fresh condensed linkage. Therefore, considering a period quite long to enable the diffusion of a pair of reactive groups, collision frequency between two functional groups will be higher for shorter polymer molecules.^[35,36]

4 | CONCLUSIONS

The molar mass of the polyol directly influences the polymerization kinetics of polyurethanes. This influence is studied in the present work using an ANN, and a SRM approaches. Also, it was selected a proper kinetic model (autocatalytic) to describe the experimental data. Nevertheless, in several situations, the models' residual error is

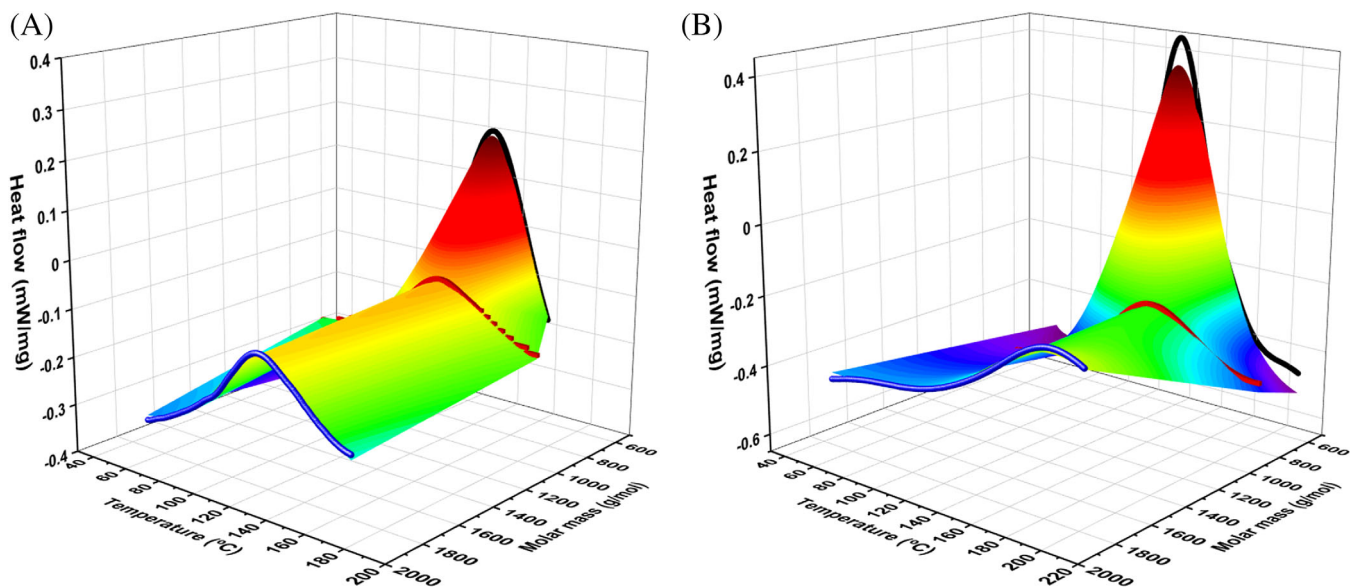


FIGURE 5 Surface response methodology (SRM) curve based on artificial neural network (ANN) dataset: (A) 10°C/min and (B) 20°C/min [Color figure can be viewed at wileyonlinelibrary.com]

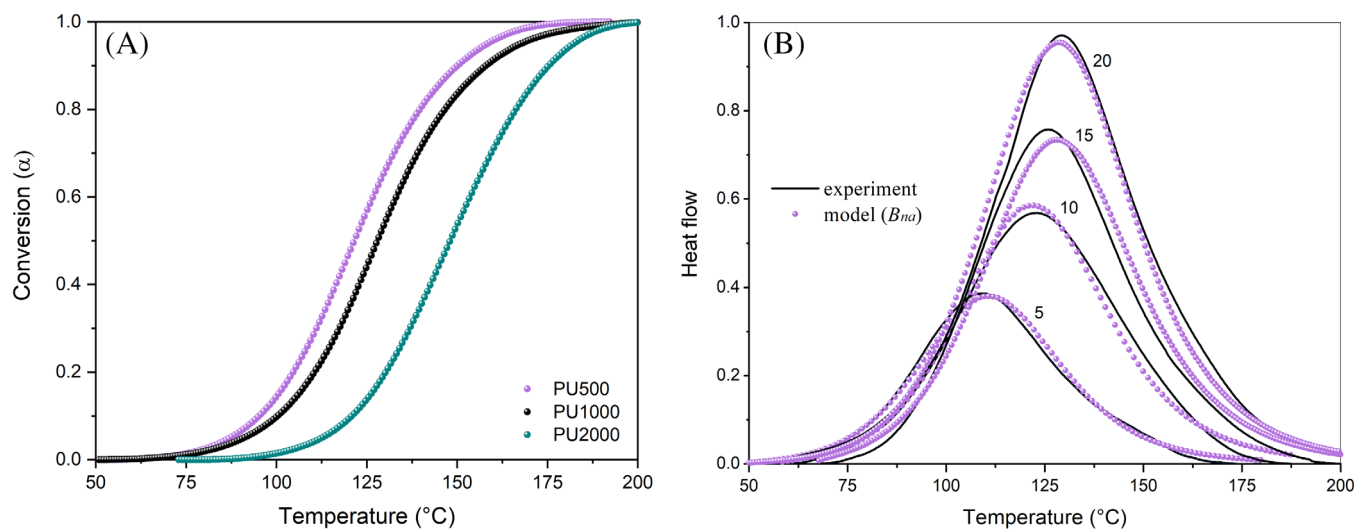


FIGURE 6 (A) Conversion in terms of temperature for the PU formulations (PU500, PU1000, and PU2000) and, (B) comparison between the differential scanning calorimetry (DSC) experimental results and those mathematically treated by the B_{na} model for PU 2000 [Color figure can be viewed at wileyonlinelibrary.com]

Sample	E (KJ/mol)	$\log A$ (1/s)	n	a	r^2	F test
PU500	46.94	4.28	1.494	0.4422	0.9857	1.00
PU1000	46.94	4.44	2.130	0.2905	0.9905	1.00
PU2000	49.39	4.20	1.204	0.3480	0.9870	1.00

TABLE 1 Values of kinetic parameters and statistical analysis by $f(\alpha) = B_{na}$

not acceptable in the whole process description. The proposed methodology becomes a powerful approach to address this kind of problem due to its lower residual errors than those obtained in individual models. With the combination of ANN and SRM, predicting the

calorimetric curves from different heating rates with a high level of reliability was possible. The simulated data were used to calculate the polyurethane's reaction kinetics, and a remarkable agreement between the modeled and experimental data was obtained. Also, it was possible

to prove that the reagents' molar mass directly influences the polyurethanes thermal response, affecting the polymerization process, the enthalpy, and the degree of reaction. The ANN proved to be an efficient tool device for simulating and predicting the tested PU's thermal behavior. ANN and SRM models allow excellent predictive abilities for any measured property since many experiments are previously performed.

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CONFLICT OF INTEREST

The authors declare that they have no conflict of interest.

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