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Research Article

New Characterization Method for the Deflation of Pabu-Type Isotropic Networks

Mohamed Salah. Mahi [1], Sofiane. Bedjaoui [2, 3,]

[1] *Department of Electrical Engineering, Technology Faculty, Tahri Mohamed University, Béchar Algeria* mahi.salah@univ-bechar.dz

[2] *Macromolecule Research Laboratory, Faculty of Sciences, University of Tlemcen, BP119, 13000, Tlemcen, Algeria*

[3] *Department of Mechanical Engineering, Technology Faculty, Tahri Mohamed University, Béchar Algeria* *bedjaoui.sofiane@univ-bechar.dz*

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ABSTRACT

After nearly three decades of development, molecular imprinting has emerged as a robust technique for the creation of selective recognition sites. Polymers have played a critical role in these advances, particularly molecular imprinting using low-molecular-weight mesogenic matrices. This study presents an innovative characterization strategy combining thermogravimetric analysis (TGA) and Fourier transform infrared spectroscopy (FTIR) to study deflation kinetics in low-molecular-weight polymer networks. This methodology allows for accurate spectral analysis of network structural changes upon template removal, establishing clear correlations between thermal behavior and molecular interactions. These insights have led to the development of a novel spectral characterization technique optimized for polymer networks that facilitates noncovalent molecular imprinting. This approach improves control over the synthesis of molecularly imprinted polymers (MIPs), providing better reproducibility in the creation of selective binding cavities. By systematically linking material properties to imprinting efficiency, this work advances the rational design of MIPs for applications ranging from biosensing to separation technologies, marking an important step in the optimization of imprinting materials.

Keywords: Molecular imprint (MIPs), Polymers, Spectral Characterization, Polymer Networks, Thermogravimetric Analysis (TGA).

1. INTRODUCTION

The swelling kinetics of an elastic body is a fundamental problem in classical physics. Gels, comprising a cross-linked elastic polymer network and a fluid that fills the interstitial space of the network, provide an excellent system to study this fundamental problem. [1-7] Therefore, the deswelling of these same networks poses a problem in their characterization by spectral methods. We have tried to show that the increase in alcohol chains promotes their swelling in the PABu polymer matrix, and makes the alcohol a good solvent, however, the longer alcohol chains are retained inside the polymer control and favor a non-covalent approach for the synthesis of molecular imprints (MIPs) [8]. In this work, we have developed two new spectral methods to highlight the affinity between PaBu networks and alcohol chains.

2. EXPERIMENTAL PART:

2.1 Materials:

The monofunctional monomer n-butyl acrylate (Abu) was obtained from Sigma-Aldrich. The crosslinking agent, a difunctional monomer called 1,6-hexanediol diacrylate (HDDA), was supplied by CrayValley (France). To initiate the radical photopolymerization reaction, 2-hydroxy-2-methyl-1-phenylpropan-1-one (Darocur 1173) from Ciba-Geigy was used. Various alcoholic solvents were provided by Sigma-Aldrich.

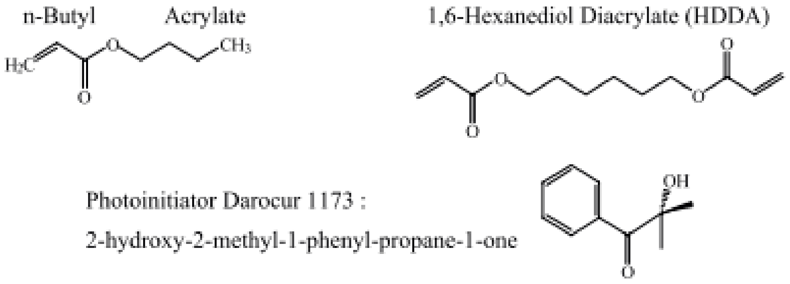

Figure 1: The chemical structures of the components of the initial mixture (before UV polymerization).

2.2 – Sample Preparation:

The Abou / HDDA / Darocur 1173 mixtures were prepared in fixed weight fractions (ABu / HDDA / Darocur 1173 / 99.4 / 0.5 / 0.5). These initial mixtures were mechanically stirred for several hours before being poured into a sample holder, presenting a single homogeneous phase.

The samples were exposed to UV radiation, under nitrogen atmosphere, using Philips TL08 UV lamps with a wavelength of 365 nm and an intensity I0 = 1.5 mW/cm2. The exposure time was set at 15 min to achieve complete conversion of all monomers in the studied system [9]. Optically the crosslinked polymer networks are transparent.

2.3- Study of deflation:

Disc-shaped samples with a diameter of approximately 3 cm were prepared. They were characterized by weight measurement using a precision balance (Mettler Toledo, 0.5 mg accuracy, 100 g max). Once the sample was polymerized and demolded, it was immersed in a container filled with a solvent. The demolded pellet was systematically weighed, following swelling kinetics that generally tended toward a plateau (to more closely approximate the thermodynamic equilibrium point). Once the plateau was reached, the samples were dried and prepared for spectral analysis.

2.4- Deflation Characterization Method:

Thermogravimetric analyses (TGA) were performed using a Pyris 1 instrument (Perkin Elmer) under a nitrogen atmosphere, up to 800°C, with a linear heating rate of 10°C min-1. FTIR spectra were recorded on a Frontier FT-IR/FIR Spectrometer (Perkin Elmer). The TGA method with a ZnSe prism was used. At least 256 scans were performed for each measurement, with a wavelength resolution of 2 cm.

3. RESULTS AND DISCUSSION:

We conducted a comprehensive study by highlighting the length of the linear alcohol chain to confirm or deny that alcohol is a good or bad solvent within the framework of the MIPs approach by studying model polymer network/solvent systems [article reference in progress]. Consequently, we showed that swelling follows second-order kinetics and that there is an affinity between PAbu networks and alcohol chains. Figure 2 shows the deswelling of these networks as a function of time. We can conclude that deswelling is complete for small chains and partial for long chains. We also observe that the kinetics of deswelling are faster than those of the swelling phenomenon, and the plateau is quickly reached, due to the mobility of the polymer chains [10]. A reversibility phenomenon is observed [11] for swelling and deswelling in the case of small alcohol chains. On the other hand, this phenomenon is not observed by the increase in alcohol chains. Tanaka et al [12] showed to analyze the deflation process was quantitative. Notably, the deflation kinetics as a function of the solvent content in the current system (PAbu + Alcohols) is totally different from that reported by Okano et al [13].

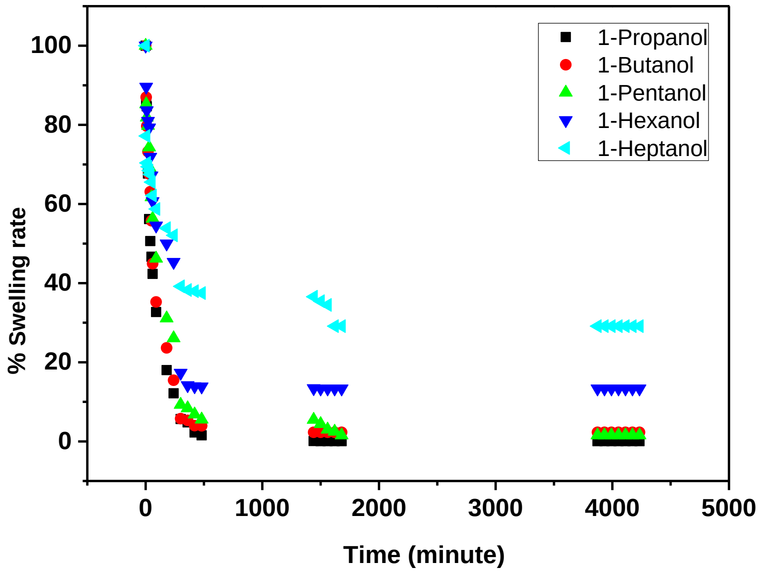

Figure 2: the deflation of the PAbu network in Alcohols

ATG was performed during the deswelling process for different chain lengths of Alcohols, Figure 3 shows the thermogram of the deswelling of PAbu in Heptanol.

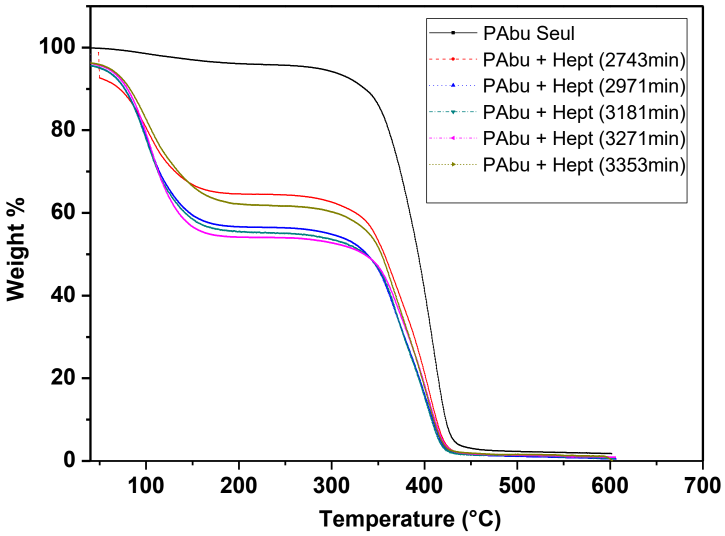

Figure 3: Thermogram of PAbu deflation in Heptanol

Figure 3 shows that after 3353 minutes of drying the heptanol remains inside the PAbu matrix, which can be explained by an affinity between the network and the long alcohol chains, to confirm this we studied an ATG for short alcohol chains, Figure 4 shows the monitoring of the deflation of the PAbu network in butanol and pentanol as a function of the drying time.

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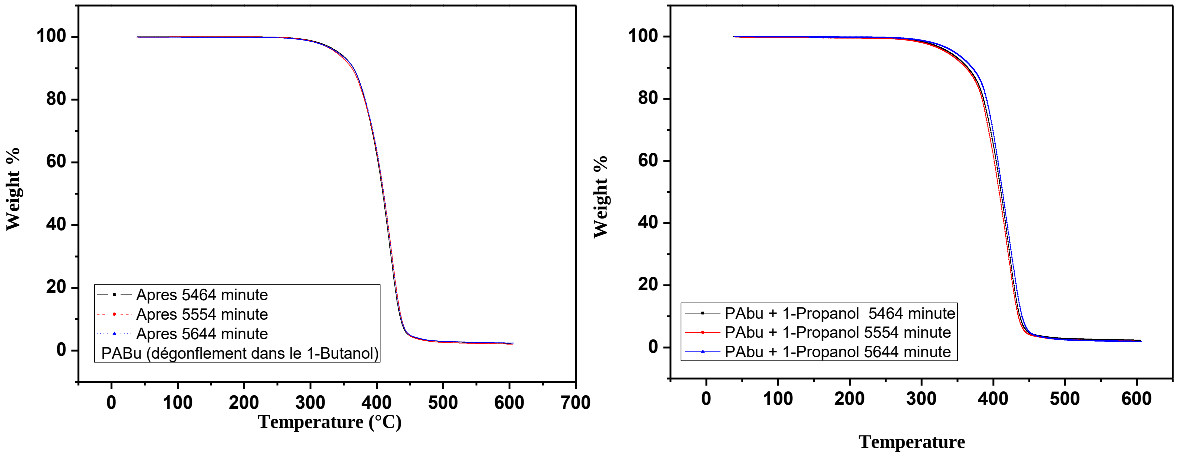

Figure 4: Thermogram of PAbu deflation in Butanol and Pentanol

Both thermograms show that there is a total deflation of the previously inflated PAbu networks, and this can perhaps explain why there is no affinity between the PAbu network and the short alcohol chains.

To better confirm the presence of alcohol chains in the PAbu network, we studied the same deflation kinetics by FTIR; Figure 5 shows the deflation spectrum of PAbu in heptanol.

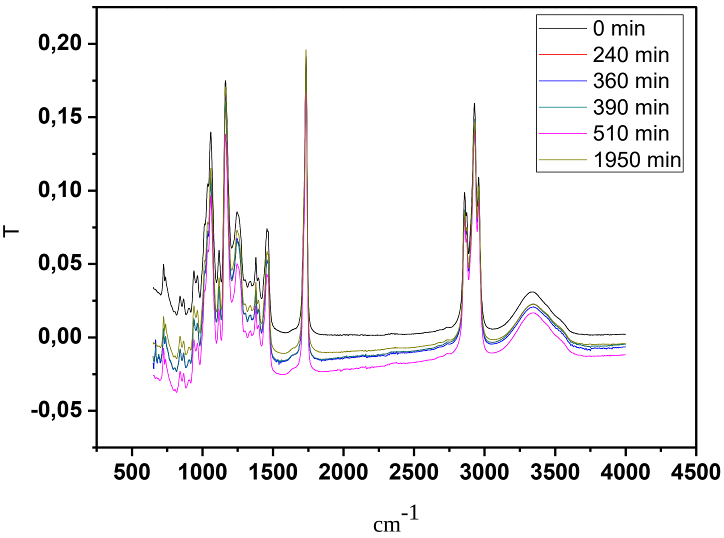

Figure 5: FTIR spectrum of PAbu deflation in heptanol.

The FTIR spectrum shows the presence of heptanol in the PAbu matrix. Indeed, at 3400 cm-1, a characteristic band is observed at the –OH group of the aliphatic chains, confirming the presence of the alcoholic chain. Therefore, we want to confirm the presence of other alcohol chains in the PAbu network. Figure 6 shows the FTIR spectrum of PAbu deflation in 1-butanol.

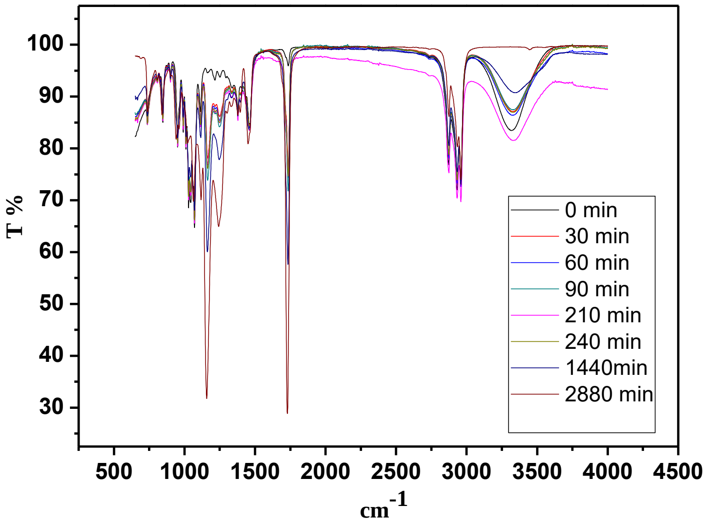

Figure 6: FTIR spectrum of PAbu deflation in 1-Butanol.

Figure 6 allowed us to conclude that the deflation is total for short alcohol chains, in fact we observe the total disappearance of the characteristic band of the –OH group at 3400 cm^{-1} and this after 2800 min of deflation.

To better see the affinity and confirm the affinity between the long alcohol chains and the isotropic PAbu network, we dried the PAbu networks under vacuum and in an oven. Figure 7 shows the thermogram of the deflation of the latter in Heptanol under vacuum and in an oven.

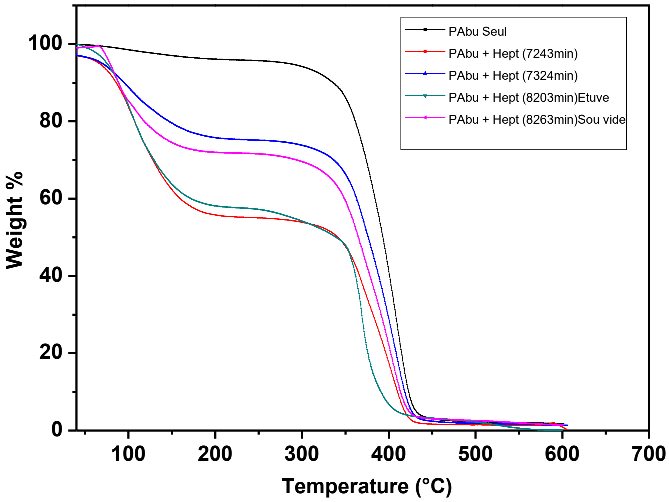

Figure 7: Thermogram of PAbu deflation in heptanol under vacuum and in the oven.

The thermogram clearly shows that there is an affinity between the PAbu isotope lattice and long alcohol chains.

4. CONCLUSION

This study convincingly demonstrates the combined value of thermogravimetry (TGA) and infrared spectroscopy (FTIR) in deciphering the deswelling mechanisms of isotropic PAbu networks in the presence of alcohols. TGA enabled precise quantification of desorption kinetics, revealing differential retention of alcohols depending on their chain length. At the same time, FTIR provided direct molecular evidence of these phenomena, confirming the persistence of hydrophobic interactions and hydrogen bonds in the case of long alcohols.

This methodological duality made it possible, at the macroscopic scale (TGA), to identify accelerated deswelling kinetics and non-reversibility linked to the steric hindrance of long chains. At the molecular scale (FTIR), it revealed the stabilization of long alcohols through specific interactions with the acrylate groups of PAbu. These insights have paved the way for rational optimization of MIPs. By correlating solvent retention (via TGA) with chemical interactions (via FTIR), it becomes possible to design imprint cavities with controlled geometries, capable of selectively targeting long-chain molecules. This methodological advance, combining thermal and spectral analysis, constitutes a key tool for the design of smart polymer materials, particularly in the fields of chemical detection or molecular purification. The TGA/FTIR alliance is thus establishing itself as a key methodology in polymer materials science.

ACKNOWLEDGEMENT

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