



X-ray absorption spectroscopy of polyureas and polyurethanes and their use in characterizing chemical gradients in thin-walled polyurea capsules

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Abstract

The carbon 1s near edge X-ray absorption spectra of several aromatic and aliphatic polyureas and polyurethanes are reported and their spectral features are assigned. An example is given of the application of these spectra as references for quantitative chemical mapping by scanning transmission X-ray microscopy (STXM) which is being used for analytical feedback in the development of controlled release polyurea capsules with chemical structuring across the capsule wall.

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1. Introduction

Microencapsulation [1] is used to isolate chemical species from the environment until they are needed for a particular application. This technology is used widely in adhesives, pharmaceuticals and agricultural products. The properties of the capsule wall must meet numerous requirements, such as being non-reactive to the species under containment and stable during storage, yet provide controlled and even triggered release in use. Polyurea capsules, formed by interfacial polyaddition between isocyanates in the dispersed phase with amines in the continuous aqueous phase, offer excellent empirical control over wall properties and release behavior. The overall goal of our research is to develop methods to study and control the chemical composition of micron-scale polyurea bilayer capsule walls, in order to provide means to optimize their compositions for specific applications. To that end, we develop synthetic methods that provide different compositions of the inner and outer walls, and explore the use of advanced spatially resolved chemical analysis techniques to characterize the resulting, ca 1 micron thick walls. In particular, we are using synchrotron based scanning transmission X-ray microscopy (STXM) since it has a suitable combination of chemical sensitivity and spatial resolution.

In order to reliably use STXM for this task, near edge X-ray absorption spectroscopy (NEXAFS) studies are required to properly understand spectral-structure relationships and to develop appropriate reference spectra which can be used in quantitative chemical mapping. The species of interest include aromatic and aliphatic urea and carbamate (urethane) compounds formed by reacting several different aromatic and aliphatic diisocyanates with alcohols to form carbamates, or with water and various amines to form ureas. While NEXAFS spectra of some aromatic urea and carbamate species have been reported previously [2,3], the present results expand the set considerably. This paper describes some of the spectroscopic aspects of this polyurea capsule project and shows how this knowledge can be useful in optimizing synthetic and analytical procedures. The detailed procedures for making gradient wall capsules as well as their characterization will be presented elsewhere [4].

2. Experimental

Capsules are formed by interfacial reactions of isocyanates in the dispersed oil phase, with water, alcohols or amines in the continuous aqueous phase. Fig. 1 shows some of the starting materials, reactions and products involved in these reactions. The desired reaction is that of the isocyanates with amines added to the aqueous phase to form ureas (1A, 3A) at the interface of the oil and aqueous phases. In addition to the reaction with amines, isocyanates can also react with water to form interme-

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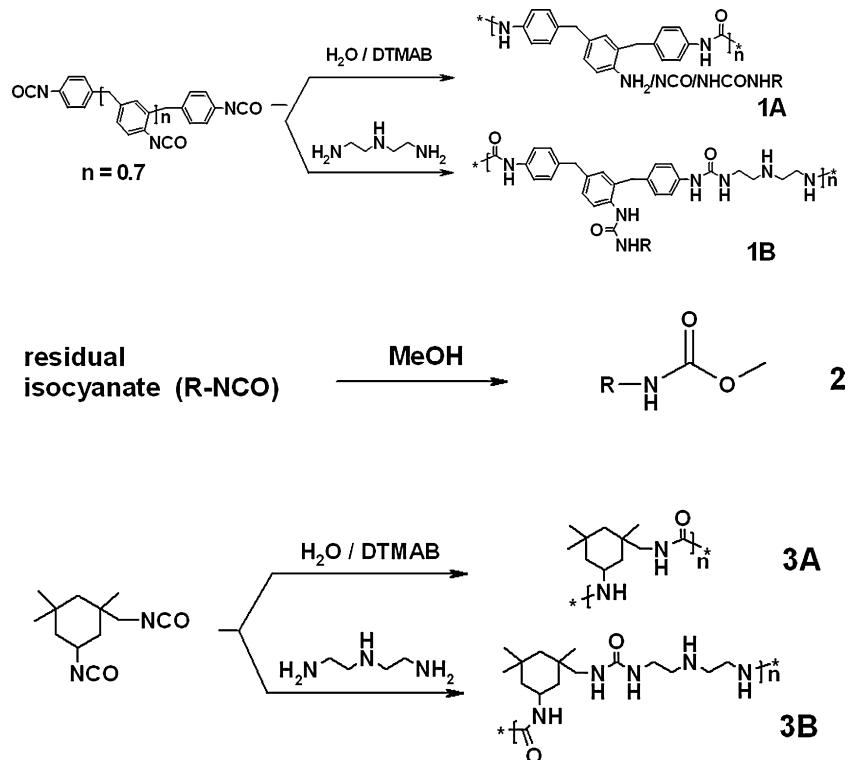


Fig. 1. Scheme of reactions involved in the interfacial synthesis and subsequent work-up of gradient wall polyurea capsules. See text for further details.

diate amines which subsequently react to form another type of urea (1B, 3B). Chemical gradients across the polymer walls may be formed if these interfacial processes take place in sequence, due to differences in diffusion rate, reactivities or both.

If there is unreacted isocyanate trapped inside the capsule, it may react with methanol used during work-up to form carbamates (2). As well, mixtures of aromatic and aliphatic isocyanates may react sequentially during encapsulation to form gradient walls.

The first process is observed in cases where the initial interfacial reaction of PMPPI with water is incomplete due to formation of dense polyurea walls that limit amine in-diffusion (1A). Methanol added during work-up can then diffuse into the cores and convert polymer-bound residual isocyanate groups, into methyl carbamate groups (2). While such groups do not serve a structural purpose, their detection would indicate the presence of significant amounts of unreacted isocyanate in capsules at the end of interfacial reactions.

The second process, sequential reaction of different isocyanates with aqueous amines, may also lead to the formation of capsule walls with a bilayer or gradient composition. Because aromatic isocyanates react more quickly than aliphatic isocyanates, the initial period of a reaction involving a mix of aliphatic and aromatic isocyanates will be dominated by formation of aromatic ureas (1B). Later, after most of the aromatic component has been consumed, the aliphatic urea (3B) will be formed. Since the reaction takes place at the oil side of the forming capsule wall, this should lead to capsules in which the outer wall consists predominantly of aromatic urea while the inner

wall is mainly aliphatic urea, with a chemical gradient across the wall.

Studying the chemical structure of capsule walls by STXM requires the preparation of ~100 nm thick cross-sections by microtomy. It is essential that the inner and outer sides of the capsule wall can be unambiguously identified in the microtomed sample. This is achieved by using methanol or tetrahydrofuran to extract the oil phase from the interior of the capsules, thereby collapsing the 50–200 μm diameter capsules in much the same way raisins are formed by dehydrating grapes.

After embedding in an amine epoxy¹ developed specifically for STXM, the subsequent microtomed sections contain loop regions (the folds of the ‘raisin’) in which the inner and outer walls can be clearly identified. Away from the loops, the walls frequently ‘twist’ during sample preparation such that the inner-outer distinction is lost.

All of the reference polyurea and carbamate (polyurethane) compounds were synthesized by solution polymerization. Aromatic and aliphatic carbamates were synthesized by reacting methylene diphenyldiisocyanate (MDI) and isophorone diisocyanate (IPDI) with 1,4-butanediol. Aromatic and aliphatic polyureas were synthesized by hydrolysis of PMPPI and IPDI. Tributylamine was added as catalyst for the synthesis of aliphatic polyurea, and the reaction was carried out at 60 °C.

¹ A 1:1 (w) combination of an aliphatic epoxy, trimethylolpropane triglycidyl ether, and an alicyclic amine, 4,4'-methylenebis (2-methylcyclohexylamine), chosen to form a pure aliphatic embedding resin without background signals in the aromatic and carbonyl regions.

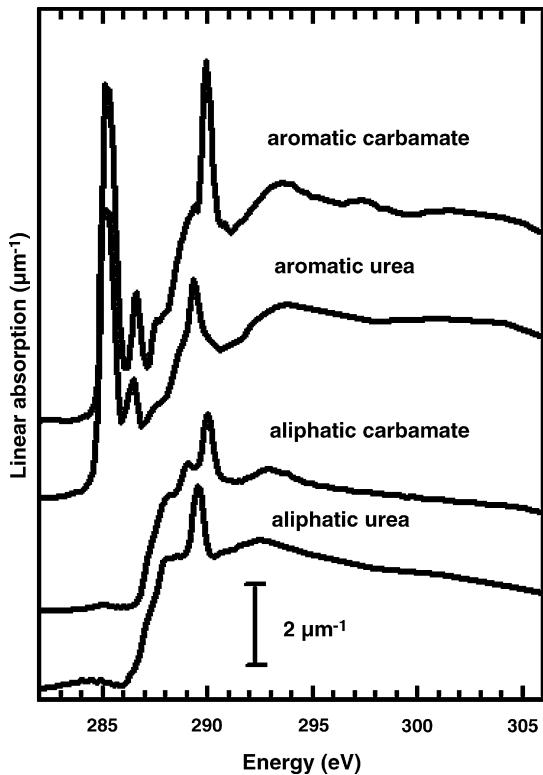


Fig. 2. C 1s NEXAFS spectra of aromatic and aliphatic polyureas and polycarbamates recorded by STXM. These spectra are of pure materials (synthesized using reactions shown in Fig. 1), embedded in an amine epoxy resin, and microtomed to ~ 100 nm thickness. The absolute linear absorption scale (OD1) is that for the response of 1 nm thickness of the material.

NEXAFS spectra and images are recorded using the STXM [5] at beamline 5.3.2 [6] at the Advanced Light Source. Acquisition and data analysis procedures have been described elsewhere [7].

3. Results and discussion

Fig. 2 presents the C 1s NEXAFS spectra of the PPMPI (aromatic) and IPPI (aliphatic) polyureas and polyurethanes (also known as polycarbamates). Energies and suggested assignments are listed in Table 1. These spectra have been placed on an

absolute linear absorption scale by matching the intensities outside of the structured near edge region to those predicted from the known elemental composition and atomic absorption coefficients [8]. The differentiation of aromatic and aliphatic species is easily made from the 285 eV peak associated with the phenyl rings of the PMPPI compounds. Differentiating the urea and carbamate species is more challenging but can be done by careful examination of the energy of the C 1s $\rightarrow \pi^* \text{C=O}$ transition, which is about 0.3 eV higher in the carbamate than the urea. This difference is associated with the increased electronegativity of the local environment of the carbonyl carbon on passing from urea (2N, 1O), to carbamate (1N, 2O). The variation of $\pi^* \text{C=O}$ transition energies with local environment has been documented previously, both experimentally and by quantum computations in condensed [9] and gas phase [10] species. Further details of the spectral assignments are presented in Table 1.

As an example of the application of these reference spectra to the development of polyurea capsule synthesis procedures, we describe the STXM analysis of SR033, a test sample designed to produce a uniform composition aromatic urea capsule wall, which was made by hydrolysis at 70 °C over 4 h of only PMPPI catalyzed by dodecyltrimethylammonium bromide (DTMAB). The aliphatic IPDI was not used. To our surprise this sample exhibited a clear bilayer structure even though it did not include the aliphatic component. Fig. 3 shows quantitative maps of the three chemical components found in this system, derived by singular value decomposition analysis of a C 1s image sequence (139 images between 278 and 340 eV, each image 113×63 pixels, 1 ms dwell/pixel). Figure 3d is a color coded composite which displays the spatial relationship of the components. Fig. 4 plots the C 1s NEXAFS spectra of the outer and inner layers, in comparison to the reference spectra for the aromatic urea and the aromatic carbamate. The NEXAFS spectra clearly indicate that the material on the inside of the capsule wall is almost pure aromatic carbamate whereas that in the well defined outer portion of the wall is aromatic polyurea. This analysis showed us that our initial procedures did not lead to complete reaction, but instead left significant amounts of unreacted isocyanate inside the capsule. As shown in the quantitative maps (Fig. 3), the capsule wall has about 50% carbamate, with the remainder being the expected urea. From this result, it was

Table 1

Energies and proposed assignments of the features in the C 1s NEXAFS spectra of the aromatic polyurea (1A), aromatic polycarbamate (2A, R from 1A), aliphatic polyurea (3A) and aliphatic polycarbamate (2B, R from 3A)

Energy	Assignment (final orbital)									
	1A	2A	3A	2B	C=C	C-R	C-H	C-C	C-O	C=O
285.14	285.17	(285.1) ^a	(285.1) ^a	(285.1) ^a	1 π^* _{ring}					
286.5	286.6					1 π^* _{ring}				
287.6	287.7	287.3 (sh)	287.3 (sh)	287.3 (sh)			C-H			
		288.2	288.2	288.2				C-H		
288.6	289.1			289.0				$\sigma^* \text{C-C}$		
289.45 ^b	289.91 ^b	289.59 ^b	289.59 ^b	289.97 ^b					$\pi^* \text{C=O}$	
293.9	293.9	293	293	292.9				$\sigma^* \text{C-C}$	$\sigma^* \text{C-O}$	
303.3	303.4	303	303	304	$\sigma^* \text{C=C}$				$\sigma^* \text{C=O}$	

^a Impurity aromatic component.

^b Estimated precision of 0.03 eV; estimated accuracy of 0.08 eV.

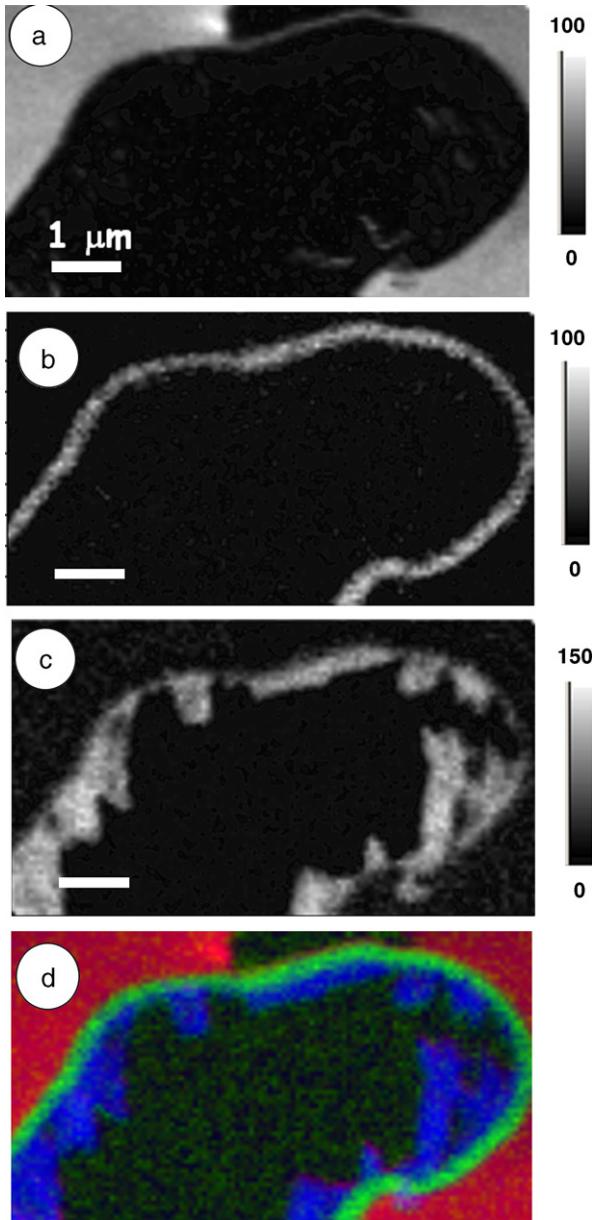


Fig. 3. Chemical component maps derived by singular value decomposition (SVD) analysis of a STXM C 1s image sequence recorded on SR033, a capsule sample aimed to form a single component, pure aromatic urea wall, in which methanol was used in the workup. (a) Epoxy, (b) aromatic polyurea, (c) aromatic carbamate; (d) color coded composite map (epoxy = red, aromatic polyurea = green, aromatic carbamate = blue. See electronic version for color).

obvious (although not realized prior to the STXM study!) that methanol was not a good choice to use for the oil extraction procedure, since, in addition to extracting the oil phase, it reacts with residual isocyanate groups to form methylcarbamates. Much of the carbamate formed is presumably polymer-bound methylcarbamate, as low-molecular weight methylcarbamates would have been removed by the extraction process. Subsequent reactions were carried out for longer periods of time to drive the initial polymerization reaction further towards completion. In addition we subsequently used only tetrahydrofuran (THF) as an unreactive extractant in the workup.

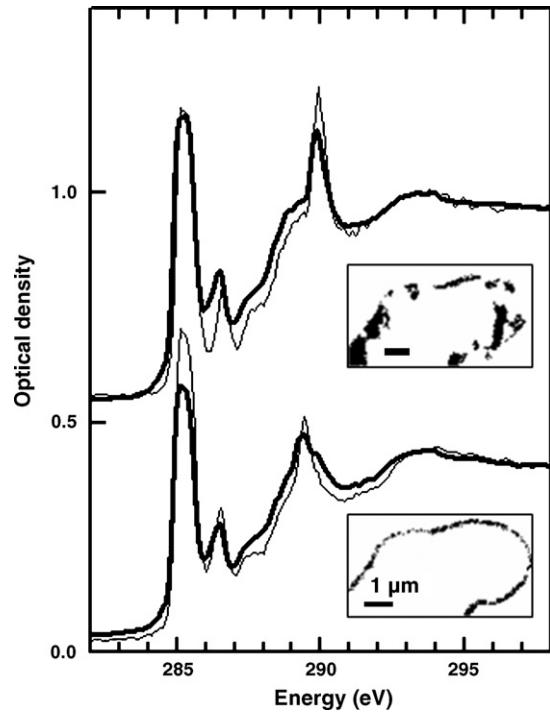


Fig. 4. C 1s spectra extracted from inner and outer regions of the capsule, specifically in the black regions indicated in the locator insert plots. The extracted spectra are plotted in comparison to the reference spectra of (upper) aromatic polycarbamate and (lower) aromatic polyurea. The OD1 reference spectra were multiplied by 80 (urea) and 72 (carbamate), which is the average thickness in nm of the sample in the selected regions. Dark lines are capsule spectra while the lighter lines are the reference spectra.

An example of successful achievement of a gradient bilayer polyurea capsule is shown by sample SR071, a capsule produced by reaction of a mixture of aromatic and aliphatic isocyanates in the oil phase with an amine cross-linker diethylenetriamine (DETA) in the water phase, followed by workup with THF to extract the core solvent and collapse the capsules. The reaction was carried out initially at 25 °C for 20 h to allow reaction of the aromatic isocyanate. Subsequently the temperature was raised to 70 °C, to accelerate the reaction of the aliphatic isocyanate. Fig. 5 displays the results of SVD analysis of a STXM C 1s image sequence (63 images between 282 and 300 eV, each image 103 × 72 pixels, 2 ms dwell/pixel). In this case there is a very clear bilayer structure with the interior of the capsule having predominantly aliphatic polyurea and the exterior of the capsule consisting of mainly aromatic polyurea, but with a detectable component of aliphatic polyurea, increasing in a gradient across the denser outer wall region. As shown in Fig. 5c, the spectrum extracted from the outer region is a very close match to the C 1s reference spectrum of aromatic urea, while the spectrum extracted from the inner region is a very close match to the C 1s reference spectrum of aliphatic urea. The match between the spectra from the capsule and the reference spectra is not perfect on account of the presence of measurable amounts of aromatic polyurea in the inner, aliphatic-rich region and aliphatic polyurea in the aromatic-rich outer wall.

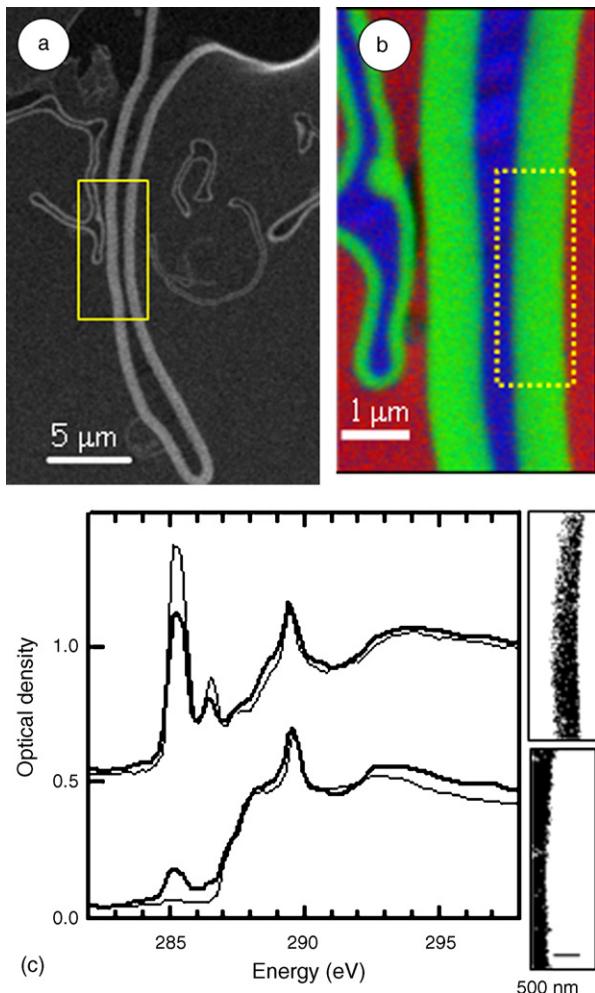


Fig. 5. (a) Overview of the region of SR071 examined. SR071 is a capsule sample with a gradient bilayer polyurea wall. (b) Color coded composite map (see electronic version for color) of 3 components derived by SVD analysis of a STXM C 1s image sequence recorded in the area indicated on Fig. 5a. (c) C 1s spectra extracted from the black regions indicated in the locator insert plots, plotted in comparison to the reference spectra of (upper) aromatic polyurea and (lower) aliphatic polyurea. The OD1 reference spectra were multiplied by 100 in each case, which is the average thickness in nm of the sample in the selected regions. Dark lines are capsule spectra while the lighter lines are the reference spectra.

Many more details of the structure of these gradient bilayer capsules, including quantitative evaluation of the gradients and more refined analysis of competing reactions, will be given elsewhere [4]. We emphasize that the examples shown in Figs. 3–5 are not intended to be a comprehensive presentation but rather are used to illustrate the way STXM-based spatially resolved NEXAFS spectroscopy, in combination with reliable reference spectroscopy, can be a powerful analytical feedback tool for optimization of synthetic and workup procedures designed to form complex, submicron-scale materials.

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