Supporting information

Thermal expansion of free volume in “classic” and regulated dimethacrylates: photocured directly and via mask to study pillar formation

Giovanni Consolati,*[a] Fiorenza Quasso,[a] Erkin Yaynik,[a] Francesco Briatico Vangosa,[b] Ondrej Šauša,[c,d] Katharina Ehrmann[e] and Helena Švajdlenková *[f]

[a] Department of Aerospace Science and Technology, Politecnico di Milano, via La Masa 34, 20156 Milano, Italy
[b] Department of Chemistry, Materials and Chemical Engineering ‘Giulio Natta’, Politecnico di Milano, Piazza Leonardo da Vinci 32 – 20133 – Milano Italy
[c] Department of Nuclear Physics, Institute of Physics of SAS, Dúbravská cesta 9, 845 11 Bratislava, Slovakia
[d] Department of Nuclear Chemistry, Faculty of Natural Sciences, Comenius University in Bratislava, Mlynská dolina, Ilkovičova 6, 842 15 Bratislava, Slovakia
[e] Institute of Applied Synthetic Chemistry, TU Wien, Getreidemarkt 9/163 MC, 1060 Vienna, Austria
[f] Department of Synthesis and Characterization of Polymers, Polymer Institute of SAS, Dúbravská cesta 9, 845 41 Bratislava, Slovakia

Correspondence to: Giovanni Consolati (E-mail: giovanni.consolati@polimi.it), Helena Švajdlenková (E-mail: helena.svajdlenkova@savba.sk)

1. Arrangement of the curing chamber with mask

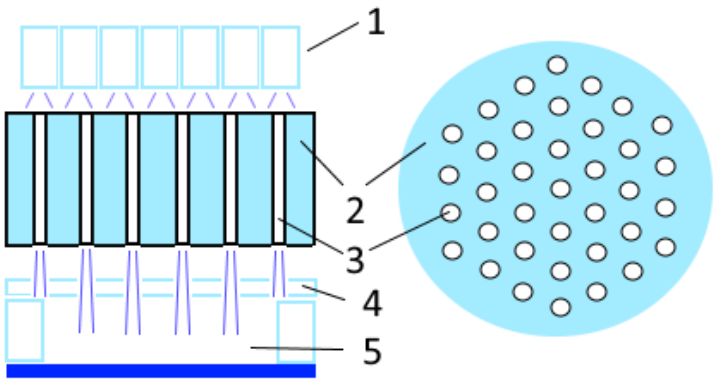

Fig. S1 A scheme of the irradiated sample through the mask. 1–LED light source, 2-Al block as a shield, 3-lightgiudes (diameter 1.1 mm, length 9 mm), 4-quartz window, 5-sample in a chamber.

2. NIR

The absorption band of N-H 1st overtone for uncured UDMA, 2M and 2M+EDDT mixtures was well decomposed by three Gaussian functions.

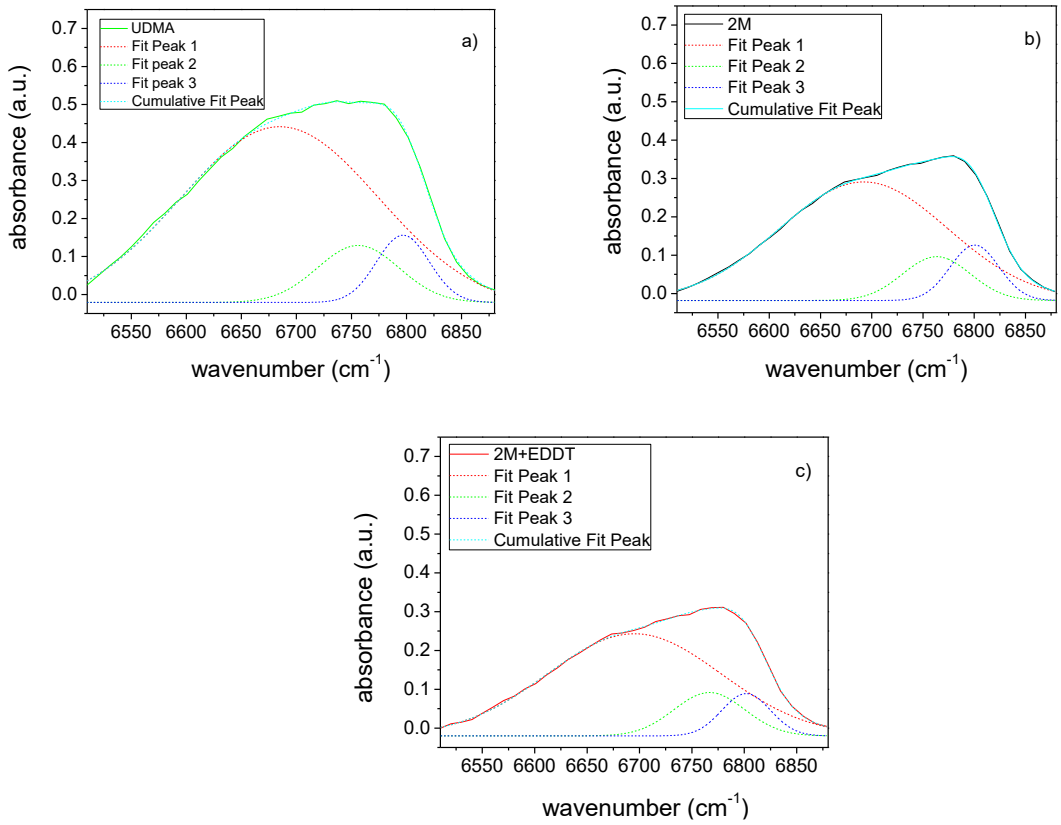

Fig. S2 Gaussian peak decomposition of the N-H absorption band for uncured a) UDMA, b) 2M and c) 2M+EDDT samples.

In Fig. S3, the comparison of >C=CH_2 absorption peak for poly2M-A and poly2M-co-EDDT samples with thicknesses (t) in the range: 2.73 – 2.83 mm (difference 0.1mm) or 2.25 – 2.49 mm (difference 0.24 mm), are shown respectively.

Based on the slight changes regarding the different thickness for both samples, the cured poly2M-co-EDDT sample exhibits higher conversion compared to the cured poly2M-A sample.

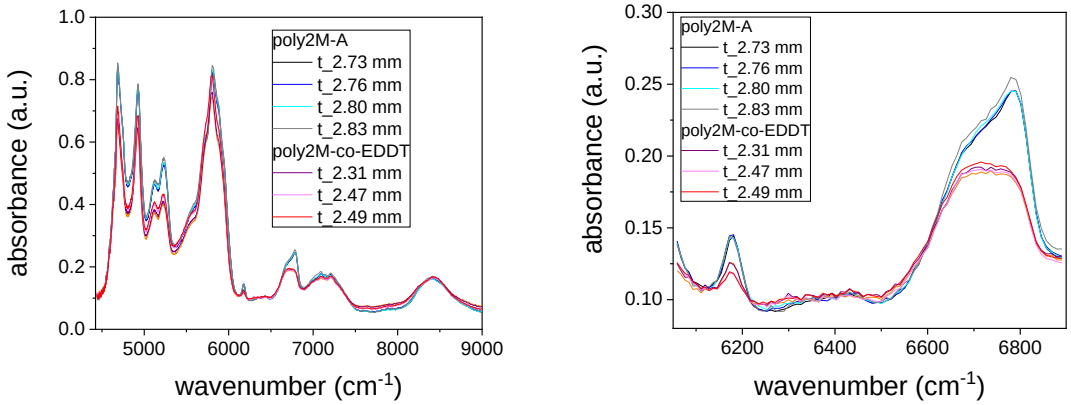

Fig. S3 NIR spectra for cured poly2M-A and poly2M-co-EDDT samples (left), measured in the middle part of discs, with detailed region of >C=CH_2 and N-H absorption peaks (right).

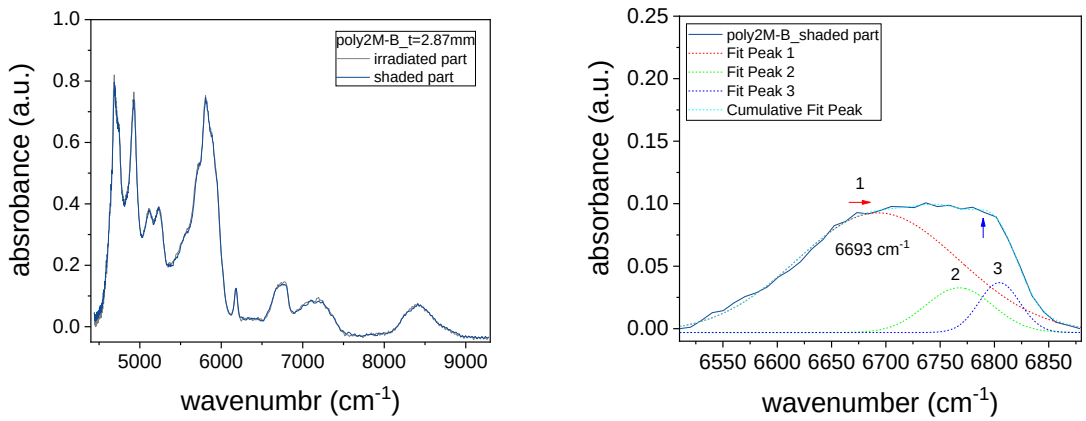

Fig. S4 NIR spectra for cured poly2M-B sample via mask (left), measured in the irradiated middle and shaded part of disc, with Gaussian peak decomposition of the N-H absorption band for the shaded part (right).

2. PALS free volume characteristics over a wide temperature range

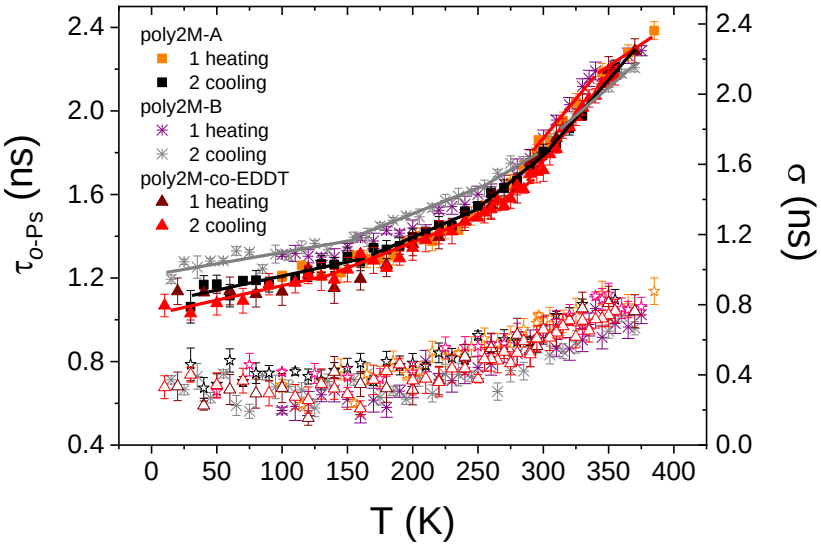

Fig. S5 Temperature dependences of the *o*-Ps lifetimes (full symbols) and the lifetime dispersions (empty symbols) for poly2M-A, poly2M-B samples and poly2M-co-EDDT. The lines show the trend of $\tau_{o\text{-}Ps}$ and σ for the cooling cycle.

The temperature dependencies of the *o*-Ps lifetimes over a wide temperature range for poly2M-A and poly2M-B show differences, mainly in the low-temperature region. The data of the cooling cycles for both samples, after first heating above 370 K, exhibited a hysteresis above room temperature. Poly2M-co-EDDT showed minimal hysteresis.

3. Local free volume properties of 2M copolymer obtained due to illumination via mask

In this PALS experiment, a positron source was sequentially placed in 6 illuminated (1) and 6 shielded (0) areas of poly2M-B sample (Fig. S6) with the collection of PALS data for five hours for each point. Both data, the angle between the measured point and the marked point on the sample surface and the radius

(distance of the measured point from the middle of the sample, i.e. zero point), define the position of the measured point.

It is important to take into account that a source of positrons ^{22}NaCl (Fig. S6, e^+ source, yellow flat disc) with an effective diameter of about 3 mm (radioactive spot) and a real implantation depth into poly2M-B of about 0.5 mm provides a rather rough area scan.[1] But the revealed trend of sequentially measured PALS data in Figure 12 a, b suggests microstructural differences of irradiated and shielded areas of poly2M-B sample.

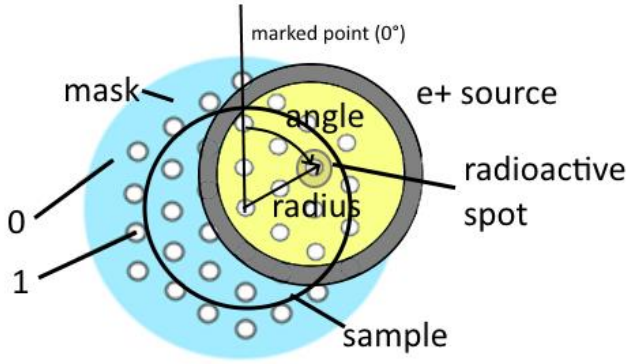

Fig. S6 The scheme of PALS measurement for directly illuminated and shielded places of cured poly2M-B sample using radioactive positron source for mapping. The measured positions on the mask. 0 – shaded area, 1 – directly illuminated area, e^+ source - ^{22}NaCl salt between two Kapton foils with radioactive spot in the middle of the disc.

Reference

1. W. Brandt and R. Paulin, *Phys. Rev. B*, 1977, **15**, 2511-2518.