D-Glucose-derived PET copolyesters with enhanced T_g

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Figure 1. ^{1}H NMR spectra of 2,4:3,5-di-*O*-methylene-D-glucitol (Glux-diol).

Figure 2. ^{1}H NMR spectra of dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester).

Figure 3. ^{1}H and ^{13}C NMR spectra of $PE_{64}Glux_{36}T$ copolyester.

Figure 4. ^{1}H and ^{13}C NMR spectra of $PET_{79}Glux_{21}$ copolyester.

Figure. 5. COSY ^{1}H-^{1}H and ^{1}H-^{13}C HETCOR NMR spectra of $PE_{64}Glux_{36}T$ copolyester.

Figure. 6. COSY ^{1}H-^{1}H and ^{1}H-^{13}C HETCOR NMR spectra of $PET_{79}Glux_{21}$ copolyester.

Figure 7. T_m values as a function of the content in Glux units.

Figure 8. SEM micrographs of films of $PE_{72}Glux_{28}T$ (a), $PE_{20}Glux_{80}T$ (b) and $PET_{79}Glux_{21}$.

Table. 1. Powder X-ray diffraction data of polyesters.

Table 2. Mechanical parameters measured in stress-strain essays.

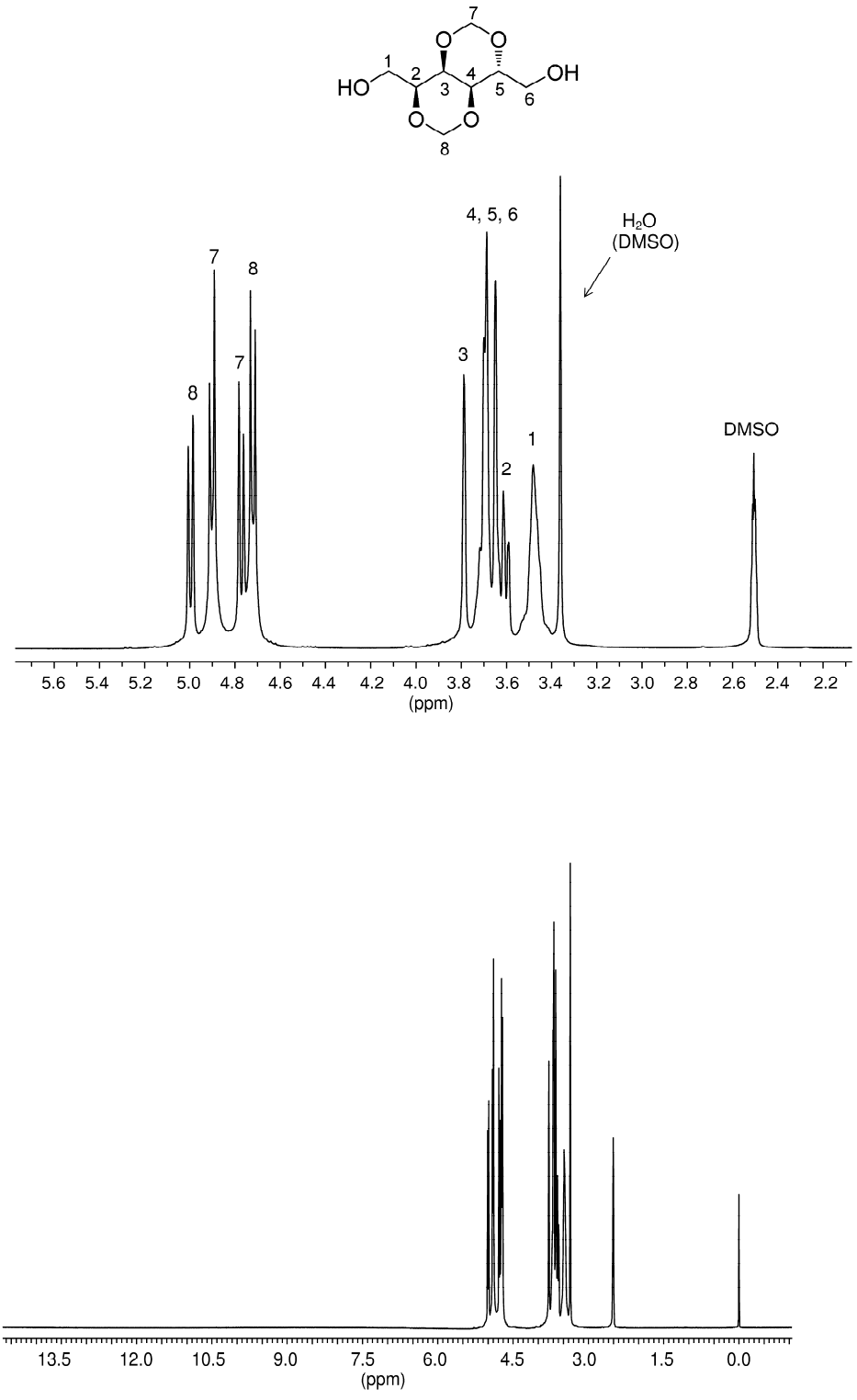

Figure 1. ^{1}H NMR spectra of 2,4:3,5-di-O-methylene-D-glucitol (Glux-diol). Bottom: The whole spectrum. Top: Enlarged region containing compound signals with assignments.

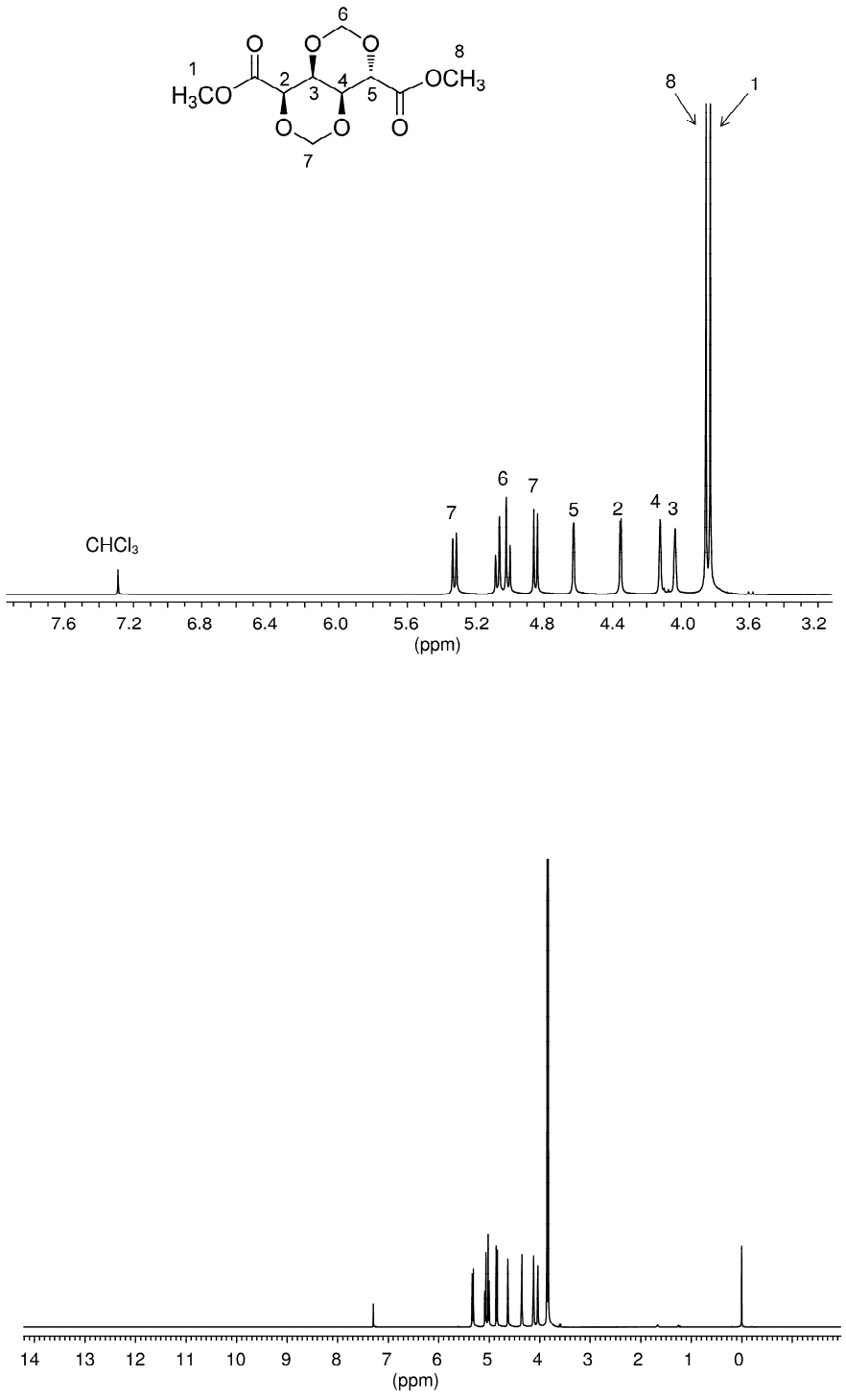

Figure 2. ^{1}H NMR spectra of dimethyl 2,4:3,5-di-*O*-methylene-D-glucarate (Glux-diester). Bottom: The whole spectra; Top: Enlarged region containing compound signals with assignments.

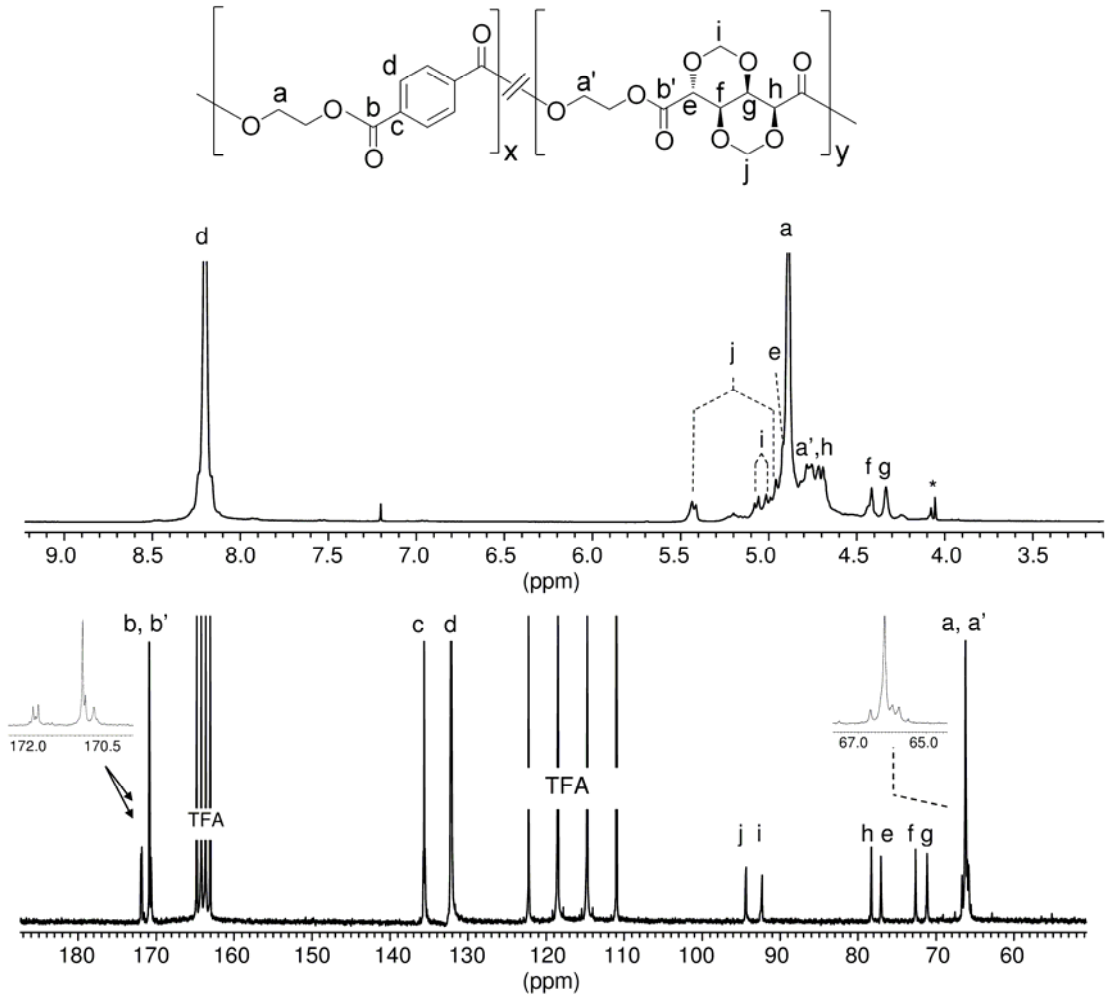

Figure 3. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $PE_{64}Glux_{36}T$ copolyester.

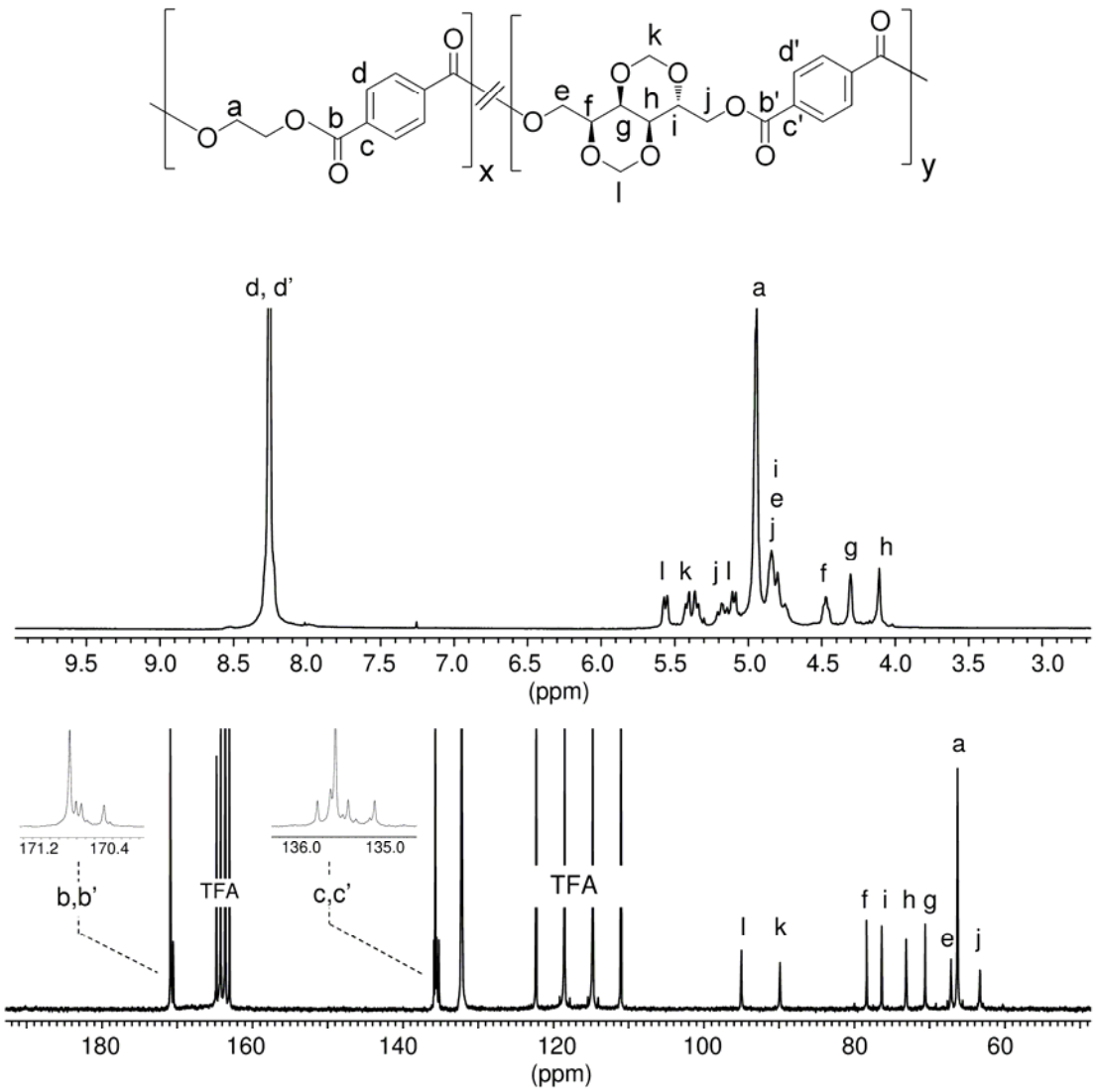

Figure 4. ^{1}H (top) and ^{13}C (bottom) NMR spectra of $PET_{79}Glux_{21}$ copolyester. (* OCH_3 end group).

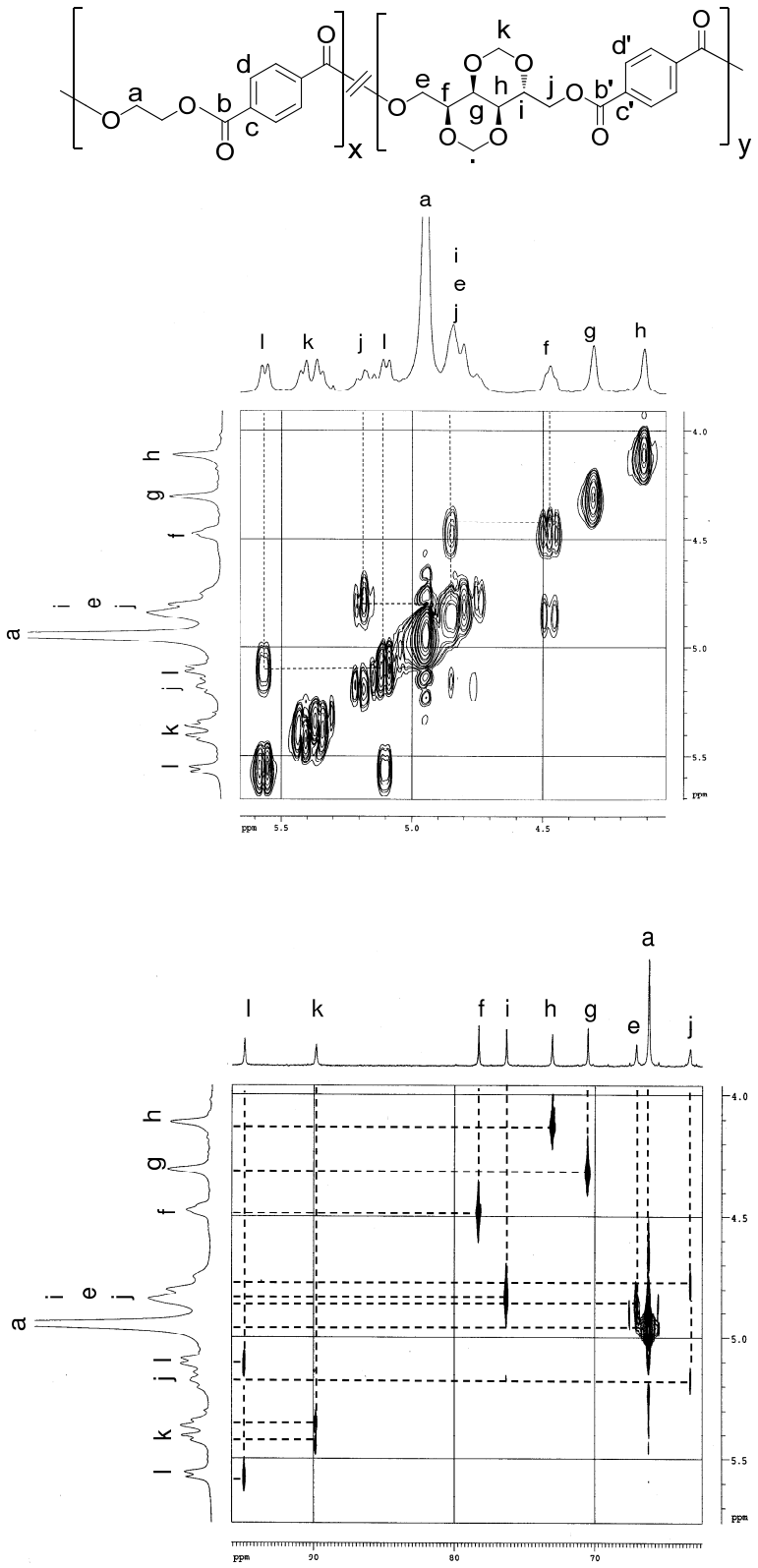

Figure. 5. a) COSY ^{1}H-^{1}H (top) and ^{1}H-^{13}C HETCOR (bottom) NMR spectra of $PE_{64}Glux_{36}T$ copolyester.

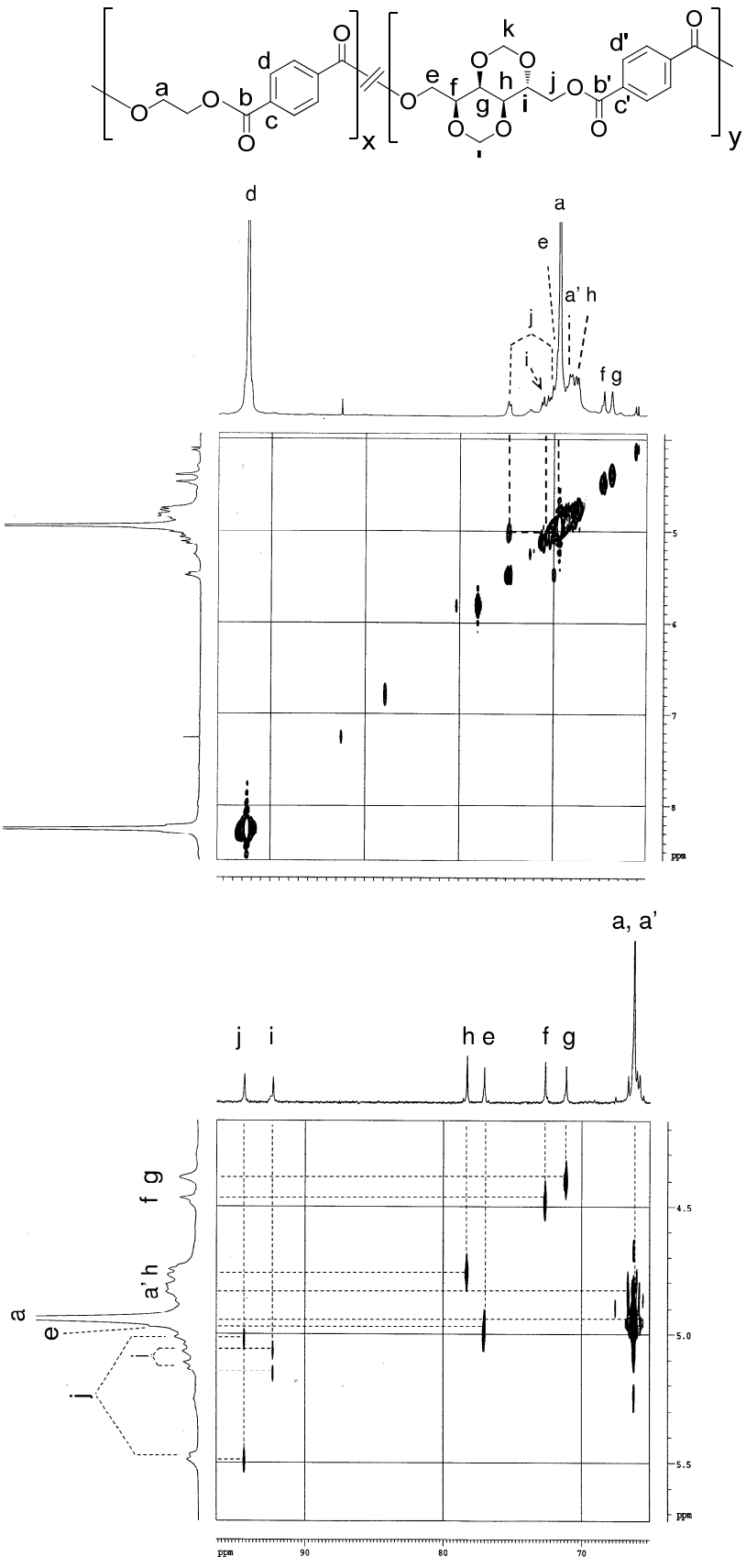

Figure 6. COSY H-^{1}H (top) and ^{1}H-^{13}C HETCOR (bottom) NMR spectra of $PET_{79}Glux_{21}$ copolyester.

Composition calculations

Although the signals corresponding to EG and Glux units are overlapped, the signal due to the aromatic terephthalate protons appears well resolved at lower field. Using the area of this signal and the area of the group of signals due to EG and Glux, it was possible to calculate the copolyester composition using the following simple expressions.

PExGluxyT :
Area of aromatic protons= K (4x+4y)
Area of EG and Glux protons= K (4x+12y)
x+y= 100

PETxGluxy :
Area of aromatic protons= K (4x)
Area of EG and sugar protons= K (4x+12y)
x+y= 100

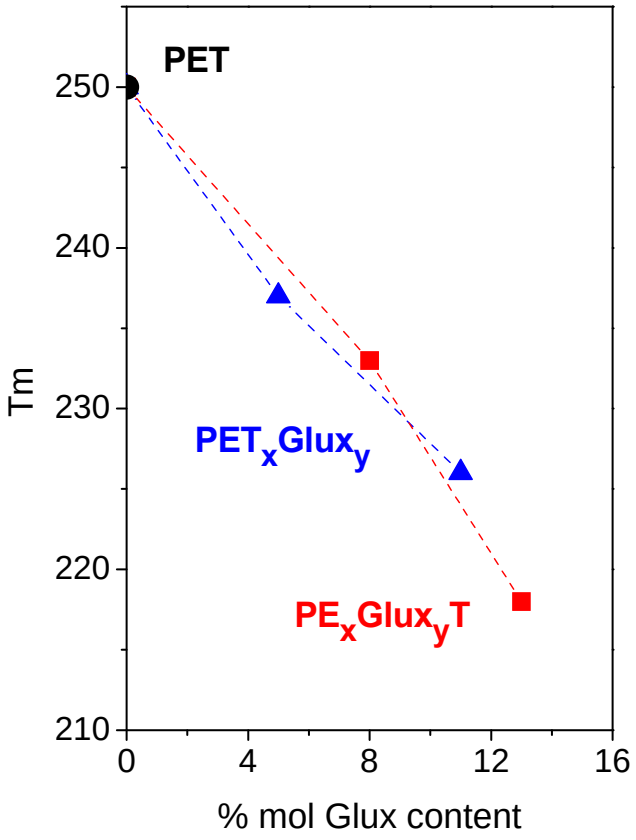

Figure 7. T_m values as a function of the content in Glux units.

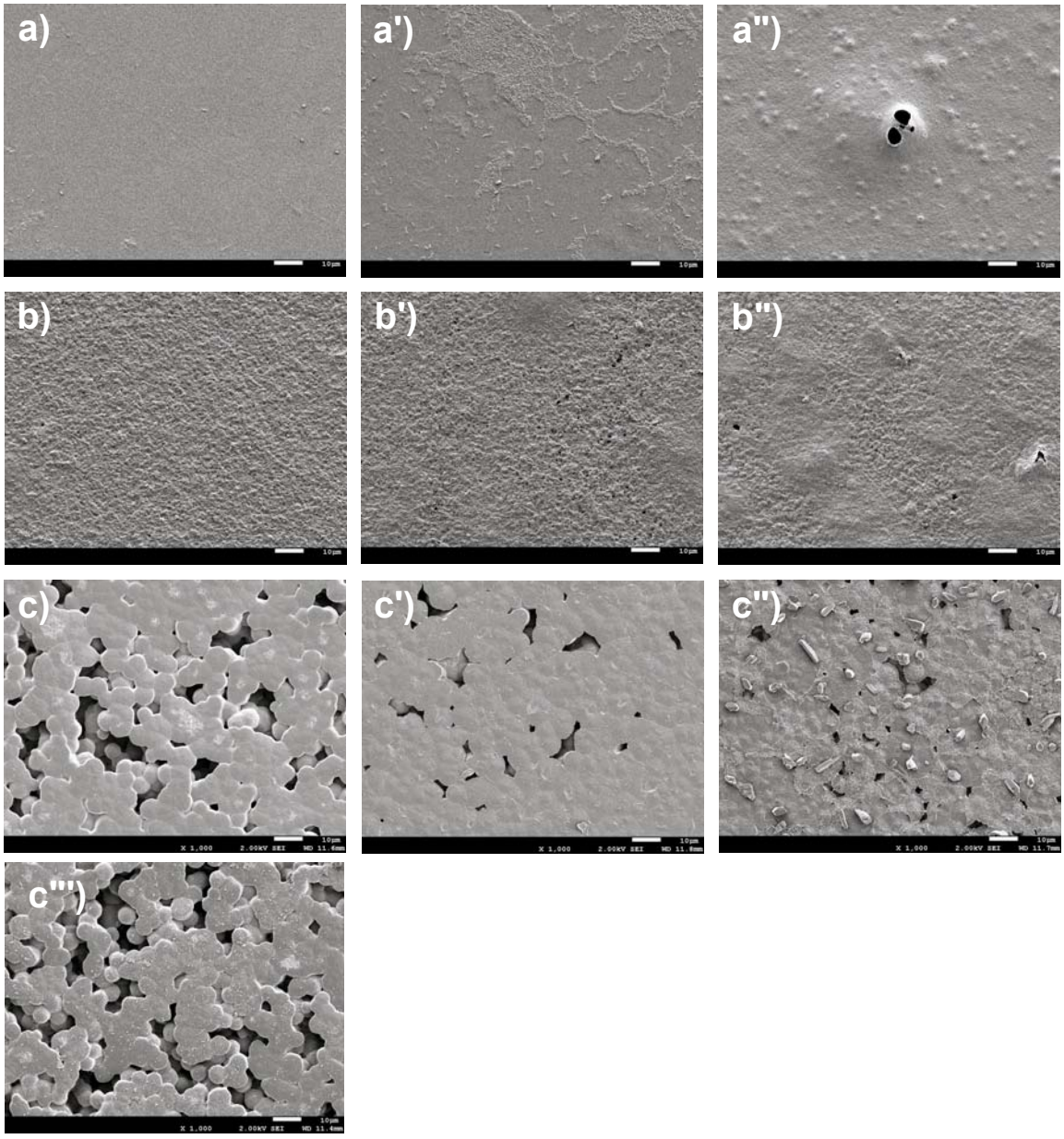

Figure 8. SEM micrographs of films of $PE_{72}Glux_{28}T$ (a), $PE_{20}Glux_{80}T$ (b) and $PET_{79}Glux_{21}$ (c). After incubation in the presence of enzymes at pH 7.4 (a',b',c'), and after hydrolytic degradation at pH 2, 80 º C (a'',b'',c''). c''': Control of and $PET_{79}Glux_{21}$ incubated at pH 7.4 but without enzymes added.

Table. 1. Powder X-ray diffraction data of polyesters.

Polyester	d_{hkl} [a] (Å)								X_c [b]
PET	5.44 s	5.00 s	4.13 s	3.91 s	3.55 w	3.40 s	3.19 m	2.72 m	0.63
$PET_{95}Glux_5$	5.43 s	5.02 s	4.13 s	3.92 s	3.55 w	3.40 s	3.19 w	2.72 m	0.45
$PET_{89}Glux_{11}$	5.43 s	5.03 s	4.14 s	3.92 s	-	3.40 s	3.19 w	2.72 m	0.37
$PE_{92}Glux_8T$	5.42 s	5.03 s	4.14 s	3.92 s	-	3.41 s	-	2.73 m	0.42
$PE_{87}Glux_{13}T$	542 s	5.03 s	4.15 s	3.92 s	-	3. 43 s	-	2.73 m	0.33

[a]Bragg spacings measured in powder diffraction patterns obtained from annealed samples. Intensities visually estimated as follows: m, medium; s, strong; w, weak.
[b]Crystallinity index calculated as the quotient between crystalline area and total area. Crystalline and amorphous areas in the X-ray diffraction pattern were quantified using PeakFit v4.12 software.

Table 2. Mechanical properties.

Copolyester	Elastic modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
PET[a]	1032±52	45±7	23±5
$PE_{79}Glux_{21}T$	1040±47	48±5	27±3
$PE_{72}Glux_{28}T$	1070±50	41±7	20±2
$PE_{64}Glux_{36}T$	1080±40	39±6	16±2

[a] Data from reference 37c in the main text.