Conformational dynamics of single molecules visualised in real time by scanning force microscope: macromolecular mobility on a substrate surface in different vapours

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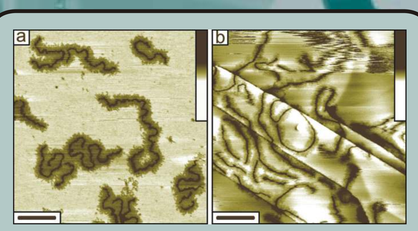
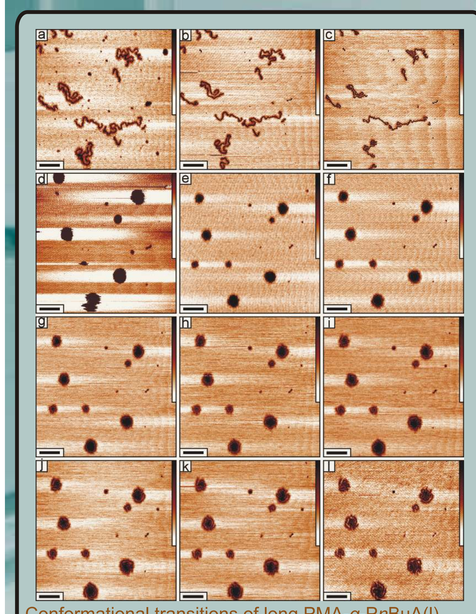
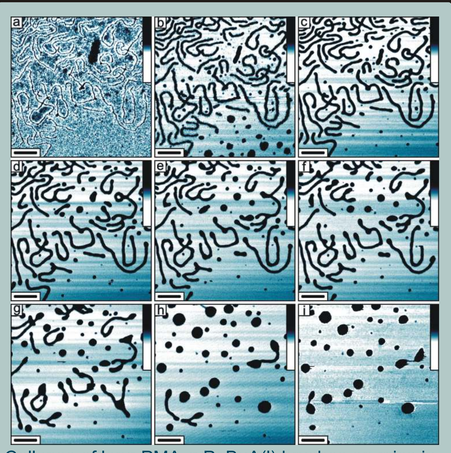


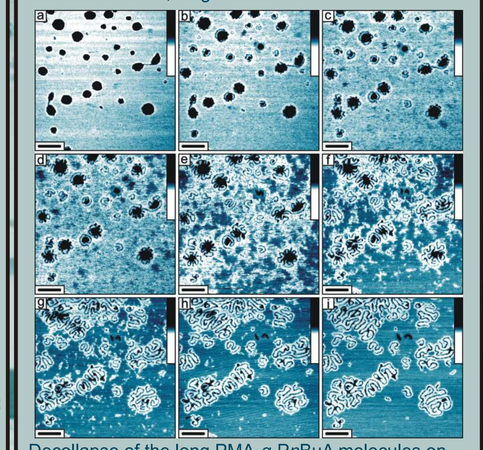
High-resolution SFM-image of PMA-*g*-P*n*BuA(l) brush molecules on mica (a) and on HOPG (b). Bar size: 150 nm, height scale: 5 nm



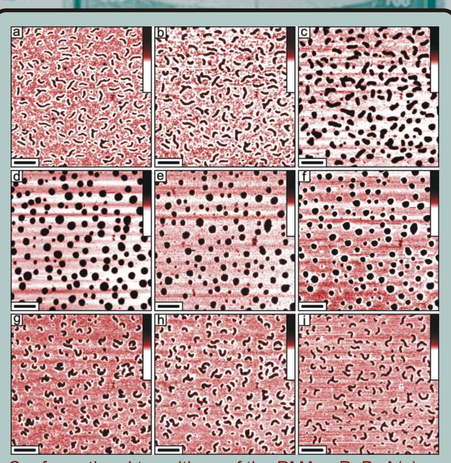
Conformational transitions of long PMA-*g*-P*n*BuA(l) macromolecules in vapours of ethyl acetate and cyclohexanone; a: initial image; b, c: images obtained after 15 min (b) and 1 h (c) exposure to ethyl acetate vapour; d: collapse induced by humidifying of the vapour; e: image in dry nitrogen; f-l: images taken after 1 h (f), 3 h (g), 6 h (h), 9 h (i), 12 h (j), 18 h (k), 60 h (l) exposure to cyclohexanone vapour. Bar: 200 nm, height scale: 2 nm



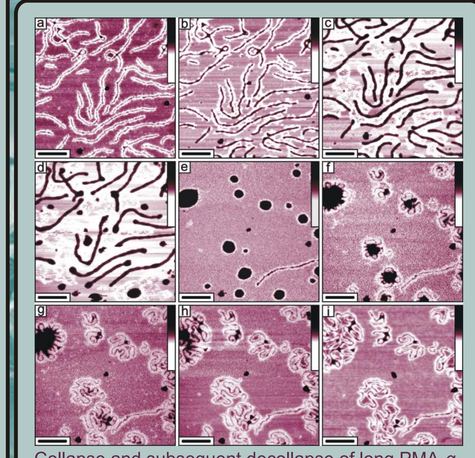
Collapse of long PMA-*g*-P*n*BuA(l) brushes on mica in ethanol vapour; a: initial image; b: image obtained after 20 min exposure to ethanol abs. vapour; c-e: images obtained 15 min (c), 30 min (d) and 1.5 h min (e) after humidifying of the ethanol vapour; f-h: images obtained 10 min (f), 15 min (g), and 25 min (h) after additional humidifying of the ethanol vapour; i: image obtained in dry N_2.
Bar size: 300 nm, height scale: 10 nm



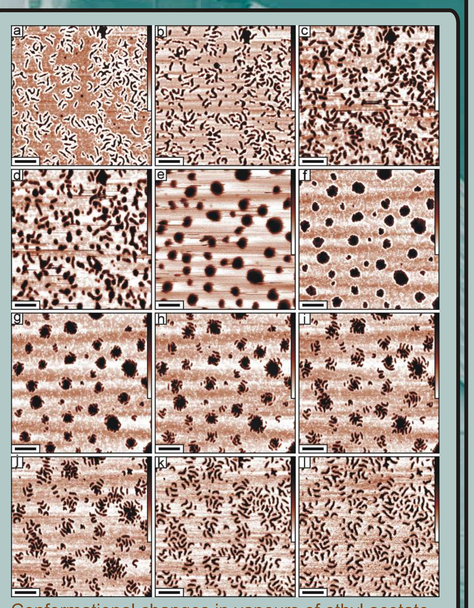
Decollapse of the long PMA-*g*-P*n*BuA molecules on mica in water vapour: images obtained after 15 min (a), 20 min (b), 30 min (c), 40 min (d), 1 h (e), 1.5 h (f), 2 h (g), 4 h (h) and 15 h (i) exposure to water vapour.
Bar size: 300 nm, height scale: 10 nm



Conformational transitions of the PMA-*g*-P*n*BuA(s) molecules on mica in ethanol and water vapours; a: initial image as deposited; b-d: images obtained after 1 min (b),15 min (c), and 25 min (d) exposure to ethanol vapour; e: image in dry N_2 atmosphere; f-i: images obtained after 1 min (f), 15 min (g), 25 min (h) and 1.5 h (i) exposure to water vapour.
Bar size: 300 nm, height scale: 10 nm



Collapse and subsequent decollapse of long PMA-*g*-P*n*BuA(l) brushes on mica in ethanol (hum.) and water vapours; a: initial image; b-d: images obtained after 10 min (b), 20 min (c), and 30 min (d) exposure to humidified ethanol vapour; e: in dry nitrogen; f-i: images recorded after 20 min (f), 40 min (g), 1 h (h) and 16 h (i) exposure to water vapour.
Bar size: 250 nm, height scale: 10 nm



Conformational changes in vapours of ethyl acetate and ethylene glycol; a: initial image; b: 1 h exposure to ethyl acetate vapour; c-e: collapse and aggregation of the individual molecules 15 min (c), 30 min (d) and 45 min (e) after the humidifying of the ethyl acetate vapour; f: drying with nitrogen; g-l: images obtained 5 h (g), 10 h (h), 15 h (i), 20 h (j), 30 h (k) and 40 h (l) after exposure to ethylene glycol vapour.
Bar size: 300 nm, height scales: 2.5-10 nm

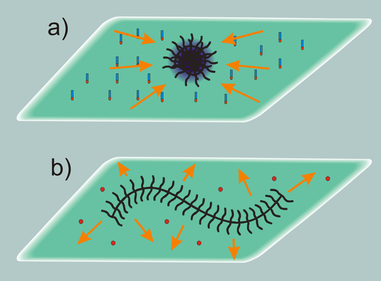
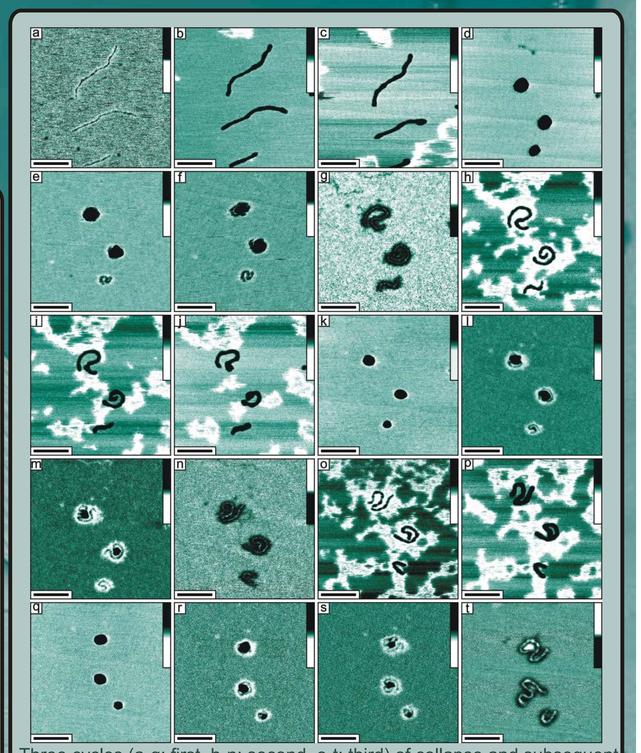


Illustration of the competition in spreading between the adsorbed polymer brush and coadsorbed molecules of a vapour phase; a: the coadsorbed layer of amphiphilic molecules has lower surface tension; b: the coadsorbed layer has higher surface tension



Three cycles (a-g: first, h-n: second, o-t: third) of collapse and subsequent decollapse for three individual brush molecules on mica in vapours saturated with ethanol (80%vol. in liquid) and water. a: Initial image; b,c,h,i,j,o,p: images obtained 10 min (o), 20 min (b,h,p), 30 min (c,i) and 40 min (j) after the exposure to humidified ethanol vapour; a,d,g,k,n,q,t: drying with nitrogen; e,f,l,m,r,s: images obtained 30 min (e,r), 40 min (f,l,s), 50 min (m) after exposure to water vapour.
Bar size: 250 nm, height scale: 10 nm

Conclusion

Environment controlled scanning force microscopy allowed to study conformational transition of single poly(methacrylate)-*graft*-poly(*n*-butyl acrylate) brush molecules on mica in real time. The molecules transform reversibly from a two-dimensional extended worm-like state to a compact globular state. The dynamics of the conformational transition has been sufficiently slow in order to allow its observation by scanning force microscope in real time. The reversible transformation is effected by coadsorption of water or ethanol from a vapour phase. The reason for the observed tendency is a competition in spreading on the substrate surface between the macromolecules and the coadsorbed vapour molecules.

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