Glass surface modification by comb-like polyethylene glycol and fluorine alkyl containing epoxide-terminated copolymers

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Intoduction

Designing the polymer nanolayers of controlled functionality, density of the packing and height on various backing surfaces is one of the promising ways for creation of composite materials with manipulated hydrophobic/lipophilic characteristics, antifouling, bactericidal or electro physical properties. In this work we consider the possibilities of glass surface modification via covalent attachment of two different types of polymers synthesized in our lab poly(polyethylene glycol methacrylate)-CGE and poly(fluorine alkyl methacrylate)-CGE of a structures presented below [1, 2]. These are comb-like polymers containing side PEG or fluorine alkyl branches and terminal reactive epoxide fragment providing addition reaction with amino group of APTES pre-immobilized on a glass surface (see the scheme).

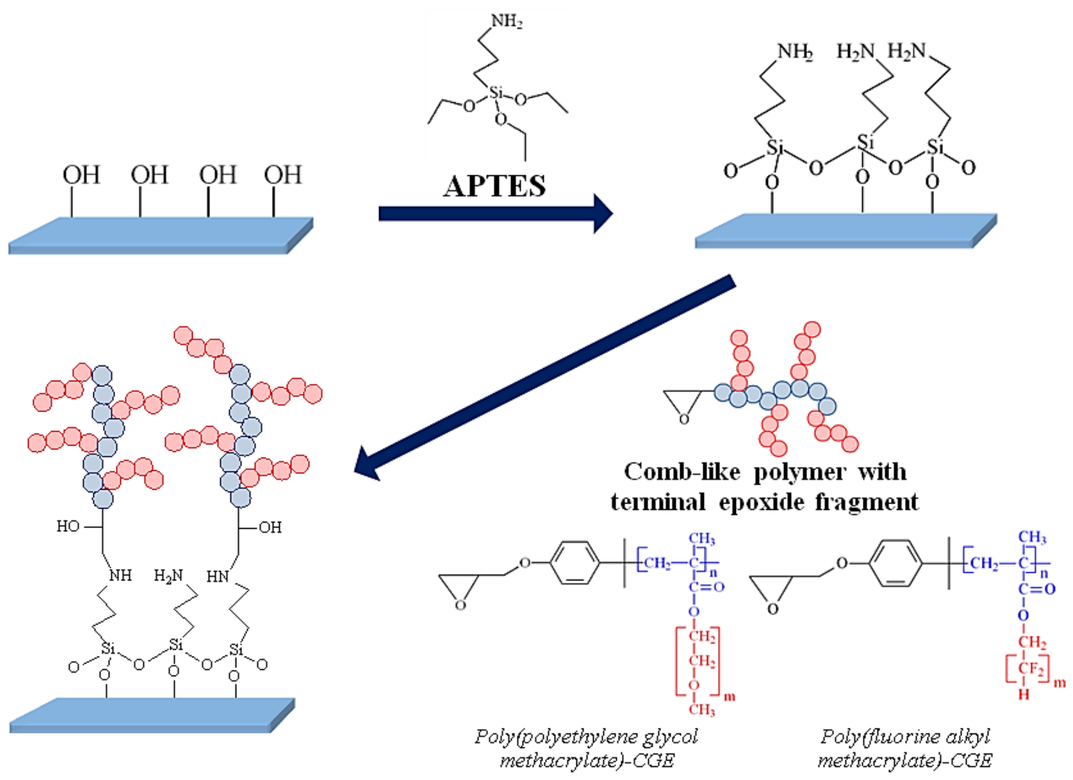

Figure 1. Schema of obtaining of polymer nanolayers.

Methods

Contact angle measurements (static water drop).

Results & Conclusions

The results of contact angle measurement of water drop on glass surface (fig. 1,2.) demonstrate significant dependences of hydrophobic/hydrophilic characteristics of modified surface not only on the natures of attached polymer but also on concentrations of the polymers in solutions, polarities of the solvent and time of aging the polymer brushes. In spite of an availability of ether Oxygen atoms in side PEG chains capable to form Hydrogen bonds with water molecules the brushes formed by poly(PEGMA)-CGE from toluene solutions are hydrophobic enough, especially after formation of the brushes from the solution of a lower polymer concentration. Moreover, the hydrophobic properties of surface characteristics aren't changed significantly after the aging during 11 days. . In our opinion, the formation of the brushes from diluted solution causes chemical adsorption of predominantly disaggregated single polymer molecules and formation of dense packing of the brushes on surface.

The decrease of contact angle of water drop on glass surface modified by poly(PEGMA)-CGE at increase of polymer concentration in solution is an evidence that brushes on the surface are formed from the polymer aggregates existing at this concentration in the solution. This defines the island structures of polymer modified surface. Moreover, specific structure of side PEG chains disposed closely along the backbone provides hydrophobic interaction between –CH2–CH2- groups and prevents fast water penetration to ether Oxygen atoms in PEG chains even after the aging. Moreover, the aging leads to the enhancement of water-repellent properties of the surface due to, probably, the increase of the interaction between PEG chains, which restricts water penetration. On contrary at low concentration of poly(F-MA)-CGE in the solution it doesn't form fully occupied surface by polymer brushes and cannot provide the same density of the brush packing in comparison with poly(PEGMA)-CGE molecules. The island structure of the brushes causes the lower hydrophobic behavior of modified surface comparing the poly(PEGMA)-CGE and defines the better water penetration between the branches. This is explained, evidently, by lower length of side fluorine-alkyl branches and the size of the polymer molecules that are chemically adsorbed onto the surface. The increase of concentration of poly(F-MA)-CGE in the solution provides the enhancement of the brush packing density and water-repellent properties of the surface. Study of the aging fluorine-alkyl brushes confirms mainly the tendency of the increase of their hydrophobic behavior at increase of polymer concentration in the solution. However, on contrary to brushes formed by poly(PEGMA)-CGE the aging the brushes of poly(F-MA)-CGE leads to negligible lowering their hydrophobic behavior due to the length and structure of fluorine-alkyl brushes on the surface that cannot provide reliable protection from penetration of water molecules. The increase of the polarity of the media of polymer solutions leads to some decrease of water-repellent properties of the polymer brushes of both types at keeping the same above mentioned general regularities.

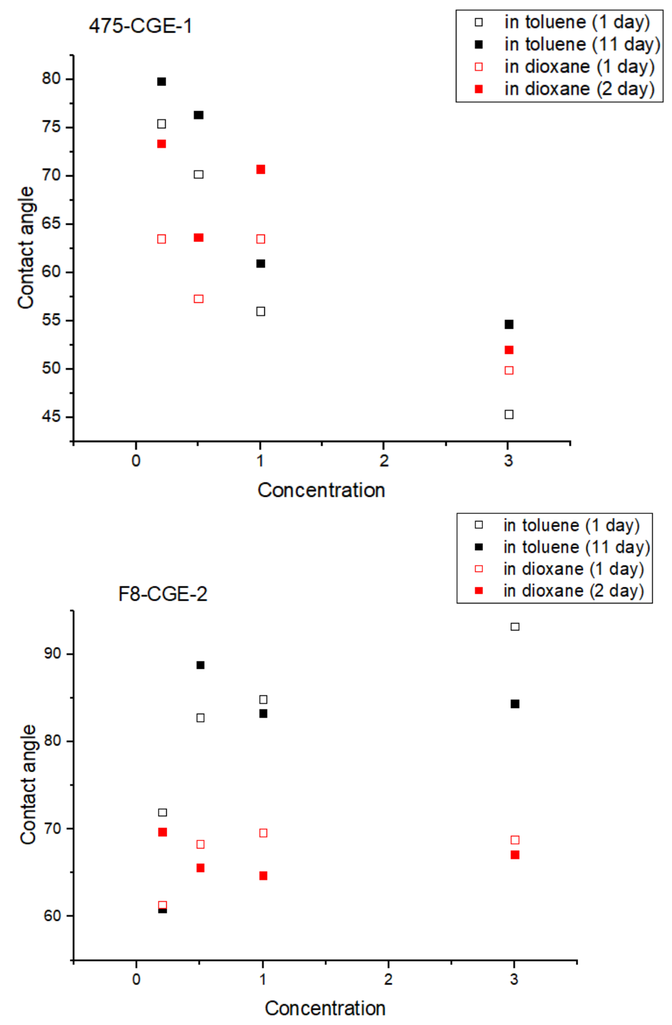

Fig. 1,2. Contact angle measurements of poly(PEGMA)-CGE (475-CGE-1) and poly(F-MA)-CGE (F8-CGE-2) tethered by ATRP in toluene and dioxane solutions.

References

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