

## Modification of polymeric materials bearing pendant epoxide groups

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The polymer containing desired functional group can be obtained by a direct-polymerization or post-polymerization modification. These functionalization methods offer different way of insertion of functionality into the polymeric materials. In the literature, scientist can meet with the descriptions of many techniques of functionalization process. This review article focuses on the pathway for post-polymerization modification of polymeric materials bearing pendant epoxide groups.

**Keywords:** epoxide group, polymeric material, modification.

### 1. INTRODUCTION

Microbeads made of cross-linked polymers can be synthesized by a range of techniques [1, 2] and play an important role in a variety of fields such as medicine and pharmaceutical applications [3], chromatography [4, 5], and organic synthesis [6]. One important parameter for the performance of microparticles in these applications is the availability of functional (polymeric) groups on the particle's surface.

Nowadays, there are two methods to receive functional polymeric material. The first one involves use of functional vinyl monomer containing pendant ester, hydroxyl, epoxy, amine, carboxylic acid, thiol,

ketone, or aldehyde group and can be polymerized directly by free-radical polymerization. In some cases obtaining of functional polymeric material by direct-polymerization is not possible because certain functionality may interfere during polymerization process. The second preferable and widely used method bases on post-polymerization modification reaction and opens a new possibilities for creating complicated structures.

## 2. POST-POLYMERIZATION MODIFIATION

The post-polymerization modification is an old technique closely connected with the history of polymer science [7]. For this purpose, several significant examples may be appealed. Hancock and Ludersdorf independently described the transformation of natural rubber into elastic material by vulcanization process with a sulfur [8], Schönbein received nitrocellulose, treating cellulose with nitric acid [9]. Cellulose was also the starting material for Schützenberger, who heated it up with acetic anhydride receiving cellulose acetate [10].

Post-polymerization modification of natural polymers was widely used in spite of the fact that the nature of such materials and their modification was misunderstood. The Staudinger's concept of macromolecules significantly changed it. Scientist also proposed the term "polymer analogous reaction" and explore these reactions as an attractive option for fabricate the functional materials [7].

The Staudinger's concept of macromolecules also maked influence on increasing use of post-polymerization modification in the synthetic polymers, for example thiol-ene addition in butadiene polymers [11], chlorination of styrene and divinylbenzene copolymers [12], halogenated poly(meth)acrylates [13], and also reaction of polymers containing epoxide group in their network [14].

The "click chemistry" idea radically changes fundamental and applied research in organic chemistry, biotechnology, medical chemistry along polymer chemistry and material science, and also has made a contribution in the expansion of this field in recent years [15–18]. This approach is an important tool in the preparation of a wide range of complex and functional macromolecular structures as well as surface modification of various materials.

The chemical transformations that fulfil stringent requirement of "click" criteria originate from four main classes of reactions [15]:

- I. cycloaddition reactions of unsaturated species, especially Huisgen 1,3-dipolar family (e.g. CuAAC, copper-catalysed azide-alkyne cycloaddition) [19], but also the (hetero) Diels-Alder reactions [20, 21],
- II. nucleophilic substitution chemistry of the ring-opening reactions of strained heterocyclic electrophiles (e.g. epoxides, aziridines, aziridinium ions, and episulfonium ions),
- III. carbonyl chemistry of the “non-aldol” type (e.g. formation of ureas, thioureas, aromatic heterocycles, oxime ethers, hydrazones, and amides),
- IV. additions to carbon-carbon multiple bonds, particularly in oxidative cases such as epoxidation, dihydroxylation, aziridination, and nitrosyl or sulfenyl halide addition, but also certain Michael-type addition reactions [22, 23].

An increasing interest has developed in the combination of “click chemistry” reactions with living/controlled radical polymerization techniques such as atom-transfer radical polymerization (ATRP), reversible addition-fragmentation chain transfer (RAFT), nitroxide-mediated polymerization (NMP), ring opening polymerization (ROP), and ring opening metathesis polymerization (ROMP) [24, 25].

### 3. NUCLEOPHILIC RING-OPENING REACTIONS

There is a broad range of suitable substrates for the ring-opening of electrophilic heterocycles including epoxides, aziridines, aziridinium and episulfonium ions, cyclic sulfates and sulfamidates and among others [7]. Materials, containing reactive epoxide groups in the polymeric network, are good starting points for readily transformation by several chemical modifications. The most commonly used and commercially available epoxy-group containing vinyl monomer is glycidyl methacrylate (GMA). It should be noted that ring-opening reaction with a nucleophile results in secondary hydroxyl groups, and may be interfere with some chemistries [2].

For the first time, systematically studied of the post-polymerization modification of GMA and glycidyl acrylate (GA)-based polymers with simple secondary amines, were done by Iwakura and co-workers in the 1960s [14, 26, 27]. The epoxide ring opening with carboxylic acids in the presence of tertiary amine (TEA) was illustrated by Kalal et.al [28].

Barbey and Klok described catalytic effect of TEA groups on nucleophilic ring-opening reactions by polyGMA-*co*-polyDMAEMA brushes preparation [29]. Ring-opening reactions with butylenediamine (BDA), diethylenetriamine (DETA), triethylenetetramine (TETA) were described by Sobiesiak and Podkościelna [30].

Relatively easy functionalization of GMA-based beads by using a single step reactions allow to introduce amine groups [31–33], quaternary ammonium functionalities [34], and sulfonic acid by sodium sulphite [35]. The epoxide groups may be also subsequently hydrolysed to afford diol functionalities [36]. Non-difficult surface modification was presented by Wang *et al.* [37] where polyethylene glycol (PEG) was coupled onto poly(GMA-DVB) microspheres to increase the hydrophilicity of the polymeric beads. Švec and Fréchet described interesting key concept about pore-size specific functionalization of macroporous particles [38]. The beads were treated with specific polymeric reagent and only those epoxy groups in larger pores hydrolysed and the remaining epoxide rings of the smaller pores were functionalized with small amine molecules.

Nowadays, for some scientist the ring opening reaction has been also investigated to make combination with other click reactions, e.g. Diels-Alder cycloaddition. The transformation of oxirane ring was conducted by the sodium cyclopentadienide, which lead to the attachment of the clickable cyclopentadienyl moieties. Grochowicz *et al.* described useful pathway of Diels-Alder reaction to modify the surface of poly(GMA-*co*-EGDMA) microspheres by maleic anhydride as a dienophile [39]. Research of Barner-Kowollik and coworkers present interesting concept of successful functionalization of hydrophobic polyGMA microparticles with strongly hydrophilic glycopolymers by combination of RAFT and hetero Diels-Alder techniques [40].

#### 4. CONCLUSIONS

The polymer containing desired functional group can be obtained by direct-polymerization or post-polymerization modification techniques. These functionalization methods offer different way of insertion of functionality into the polymeric beads. Post-polymerization modification of polymeric material bearing pendant epoxy ring, in the simple way allows to enter an interesting thiol, hydroxyl, sulfonyl, amine groups or even more complex molecular structure like as glycopolymers.

Beads with carbonyl and hydroxyl groups are used in a great variety chromatography applications and as the anchoring moieties in supports for solid phase syntheses. Those with weak basic diethylamino groups, strong basic quaternary ammonium functionalities, and strongly acidic containing sulfonic acid groups play important role as ion exchangers.

## REFERENCES

- [1] R. Ashady, *J. Microencapsulation*, **5** 101-114 (1988).
- [2] M. T. Gokmen and F. E. Du Prez, *Prog. Polym. Sci.*, **37** 365-405 (2012),
- [3] K. Saralidze, L. H. Koole, and M. L. W. Knetsch, *Materials*, **3** 3537-3564 (2010).
- [4] M. Beneš, D. Horák, and F. Švec, *J. Sep. Sci.*, **28**, 1855-1875, (2005)
- [5] B. Gawdzik and J. Osypiuk, *Chromatographia*, **54**, 595-599, (2001)
- [6] L. Sinigoi, P. Bravin, C. Ebert, N. D'Amelio, L. Vaccari, L. Ciccarelli, S. Cantone, A. Basso, and L. Gardossi, *J. Comb. Chem.*, **11**, 835-845, (2009)
- [7] K. A. Günay, P. Theato and H.-A. Klok, *J. Polym. Sci. A: Polym. Chem.*, **51**, 1-28, (2013)
- [8] W. A. Cunningham, *J. Chem. Edu.*, **12**, 120-124, (1935)
- [9] R. E. Oesper, *J. Chem. Edu.*, **6**, 677-685, (1929)
- [10] D. G. Barkalow, R. M. Rowell, and R. A. Young, *J. Appl. Polym. Sci.*, **37**, 1009-1018 (1989)
- [11] G. E. Serniuk, F. W. Banes, and M. W. Swaney, *J. Am. Chem. Soc.*, **70**, 1804-1808, (1948)
- [12] K. W. Pepper, H. M. Paisley, and M. A. Young, *J. Am. Chem. Soc.*, **70**, 4097-4105, (1953)
- [13] W. Kern, R. C. Schutz, and D. Braun, *J. Polym. Sci.*, **48**, 91-99, (1960)
- [14] Y. Iwakura, T. Kurosaki, and N. Nakabayashi, *Makromolekul. Chem.*, **44-6**, 570-590, (1961)
- [15] H. C. Kolb, M. G. Finn, and K. B. Sharpless, *Angew. Chem. Int. Ed.*, **40**, 2004-2021, (2001)
- [16] J. E. Moses and A. D. Moorhouse, *Chem. Soc. Rev.*, **8**, 1249-1262, (2007)
- [17] H. C. Kolb and K. B. Sharpless, *Drug. Discov. Today*, **8**, 1128-1137, (2003)
- [18] G. C. Tron, T. Pirali, R. A. Billington, P. L. Canonico, G. Sorba, and A. A. Genazzani, *Med. Res. Rev.*, **2**, 278-308, (2008)
- [19] R. Huisgen, *Pure Appl. Chem.*, **61**, 613-628, (1989)
- [20] M. A. Tasdelen, *Polym. Chem.*, **2**, 2133-2145, (2011)
- [21] C. Tarducci, J. P. S. Badyal, S. A. Brewer, and C. Willis, *Chem. Commun.*, 406-408, (2005)

- [22] A. S. Goldmann, A. Walther, L. Nebhani, R. Joso, D. Ernst, K. Loos, C. Barner-Kowollik, L. Barner, and A. H. E. Müller, *Macromolecules*, **42**, 3707-3714, (2009)
- [23] D. P. Nair, M. Podgórski, S. Chatani, T. Gong, W. Xi, C. R. Fenoli, and C. N. Bowman, *Chem. Mater.*, **26**, 724-744, (2014)
- [24] D. Quémener, T. P. Davis, C. Barner-Kowollik, and M. H. Stenzel, *Chem. Commun.*, **48**, 5051-5053, (2006)
- [25] W. H. Binder and C. Kluger, *Macromolecules*, **37**, 9321-9330, (2004)
- [26] Y. Iwakura, T. Kurosaki, and Y. Imai, *Makromolekul. Chem.*, **86**, 73-79, (1965)
- [27] Y. Iwakura, T. Kurosaki, N. Ariga, and T. Ito, *Makromolekul. Chem.*, **97**, 128-138, (1966)
- [28] J. Kálal, F. Švec, and V. Maroušek, *J. Polym. Sci. Polym. Symp.*, **47**, 155-166, (1974)
- [29] R. Barbey and H.-A. Klok, *Langmuir*, **26**, 18219-18230, (2010)
- [30] M. Sobiesiak and B. Podkościelna, *Key Eng. Mater.*, **605**, 173-176, (2014)
- [31] S. Paul and B. Rånby, *J. Polym. Sci. Polym. Chem. Ed.*, **14**, 2449-2461, (1976)
- [32] J. Kálal, E. Kálalová, L. Jandová, and F. Švec, *Angew. Makromol. Chem.*, **115**, 13-22, (1983)
- [33] B. F. Şenkal and N. Biçak, *React. Funct. Polym.*, **49**, 151-157, (2001)
- [34] J. Hradil and F. Švec, *Polym. Bull.*, **14**, 265-270, (1985)
- [35] F. Švec, M. Bareš, J. Zajíc, and J. Kálal, *Chem. Ind.*, **159**, (1977)
- [36] H. Hrudková, F. Švec, and J. Kálal, *Brit. Polym. J.*, **9**, 238-240, (1977)
- [37] R. Wang, Y. Zhang, G. Ma, and Z. Su, *Colloids Surf. B*, **51**, 93-99, (2006).
- [38] V. Šmigol, F. Švec, and J. M. J. Fréchet, *Macromolecules*, **26**, 5615-5620, (1993)
- [39] M. Grochowicz, P. Pączkowski, and B. Gawdzik, *Adsorpt. Sci. Technol.*, **33**, 677-684, (2015)
- [40] M. Kaupp, A. P. Vogt, J. C. Natterodt, V. Trouillet, T. Gruending, T. Hofe, L. Barner, and C. Barner-Kowollik, *Polym. Chem.*, **3**, 2605-2614, (2012)