

# ABSTRACTS



# POSTER CONTRIBUTIONS

## AZIDE/ALKYNE-"CLICK"- REACTIONS ON AMINO-RESINS: AN LC-ESI-TOF ANALYSIS

HAITHAM BARQAWI AND WOLFGANG H. BINDER<sup>†</sup>

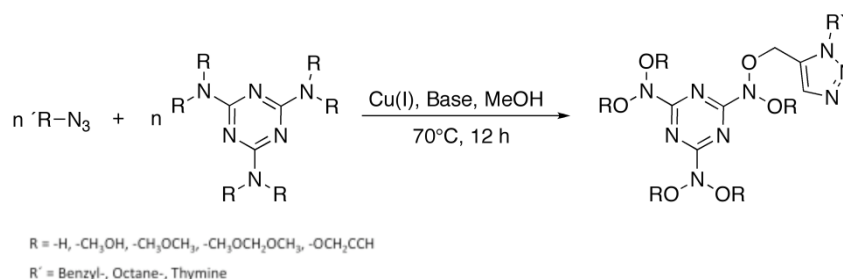
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### Abstract

The copper-catalyzed cycloaddition of azides to alkynes is one of the most significant synthetic routes to 1-substituted-(1,2,3)-triazoles<sup>1</sup>, resulting in the efficient attachment of functional additives to polymers and resin materials. Technically, the azide/alkyne-"click"-reaction also enables the efficient crosslinking of precondensates, yielding duroplastic materials with a high crosslinking density.<sup>2</sup> We here report on the application of the copper (I) catalyzed azide/alkyne-"click"-reaction onto amino-resins aiming at an efficient and cheap functionalization of melamine-formaldehyde-based resin materials.

Melamine-formaldehyde resins (MF-resins)<sup>3-5</sup> linked to terminal alkynes were prepared by addition of propargylic alcohol (1- 30 mol %) directly into the condensation process. Due to the structural diversity of the generated compounds, the alkyne-containing structures within the melamine-formaldehyde resins were characterized using high performance liquid chromatography coupled to electrospray ionization time-of-flight mass spectrometry (HPLC-ESI/TOF MS). Consequently, new chromatographic peaks were identified and a simultaneous characterization and quantification of at least compounds with mono-, di, tri-, acetylenic moieties bound to melamine-residues were unveiled. Additionally, a rough quantification of the different alkyne-containing-species could also be achieved using LC-ESI-TOF methods.

The so prepared, alkin-containing MF-resins were reacted with various organic azides such as 1-(3-azido hexyl)thymine, benzyl azide and octane azide in excess using different copper(I)-species (Scheme 1). The "clicked" structures again could be assigned and simulated using Bruker data analysis software after LC-ESI-TOF-analysis enabling an exact assignment via isotopic-pattern simulation of the m/z-values of the corresponding compounds. Thus it is demonstrated that the HPLC-ESI/TOF MS method is suitable for analysis of the complex-alkyne-MF species and the resulting triazoles after the "click"-reaction.



Scheme 1

- 1) Binder, W. H.; Sachsenhofer, R., *Macromol. Rapid Commun.*, **2008**, 29, (12-13), 952-981.
- 2) Liu, Y.; David D. Di'az; Accurso, A. A.; Sharpless, K. B.; Fokin, V. V.; Finn, M. G., *J Polym Sci Part A: Polym Chem*, **2007**, 45, 5182-5189.
- 3) Chang, T. T., *Anal. Chem.*, **1994**, 66, (19), 3267-3273.
- 4) Binder, W. H.; Dunky, M.; Jahromi, S., *Kirk Othmer Encyclopedia of Chemical Technology (5th Edition)*, **2005**, 15, 773-796.
- 5) Binder, W. H.; Dunky, M., *Encyclopedia of Polymer Science and Technology*, **2004**, 10, 369-384.

## “CLICK CHEMISTRY”: AN EFFICIENT TOOL FOR STEP GROWTH POLYMERIZATION

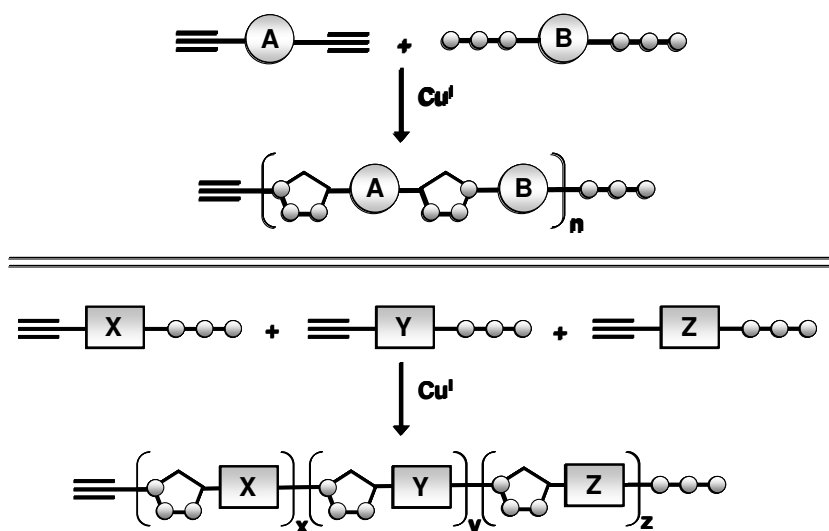
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### Abstract

The Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition (CuAAC) of an azide and an alkyne, often assimilated to “click chemistry”, has been extensively applied to the different fields of polymer chemistry and materials science since its introduction in 2002 by Sharpless and Meldal groups. Indeed, it has allowed the synthesis and functionalization of a wide range of advanced macromolecular architectures using mild and tunable conditions.<sup>1</sup>

In our group, we decided to investigate in detail the application of click chemistry reaction as a tool for step growth polymerization, through two complementary strategies based on homo- or heterofunctional monomers, i.e. AA/BB or A-B, respectively.<sup>2,3</sup> Therefore, a library of linear polytriazoles were synthesized either from dialkyne and diazide or  $\alpha$ -azide- $\omega$ -alkyne low molar mass monomers. The resulting polymers were thoroughly characterized by several techniques (i.e. <sup>1</sup>H and <sup>13</sup>C NMR, SEC, DSC, TGA), which revealed high molecular weights as well as good thermal properties, demonstrating the efficiency of the click polyaddition process. Particularly, the A-B strategy yields polytriazole (co)polymers with easily adjustable structures and properties. Moreover, further characterizations by in-situ <sup>1</sup>H NMR analyses allowed the optimization of the experimental conditions and highlighted the influence of parameters such as temperature or chemical nature and content of the catalytic system on the reaction kinetics and the properties of the resulting materials. . The impact of the dilution conditions on the molar mass and microstructure of the resulting polytriazoles was also studied by <sup>1</sup>H NMR and SEC analyses.



Scheme 1. Click Chemistry step growth polymerization via AA-BB and AB strategies

<sup>1</sup> Meldal M., Tornøe C.W. *Chem. Rev.* **2008**, *108*, 2952.

<sup>2</sup> Binauld S., Boisson F., Hamaide T., Pascault J.-P., Drockenmuller E., Fleury E. *J. Polym. Sci. Part A: Polym. Chem.* **2008**, *46*, 5506.

<sup>3</sup> Binauld S., Damiron D., Hamaide T., Pascault J.-P., Fleury E., Drockenmuller E. *Chem. Commun.* **2008**, 35, 4138.

## CLICK CHEMISTRY GRAFTING OF POLYMER (PSEUDO)-BRUSHES TO ALKYNE FUNCTIONALIZED SUBSTRATES

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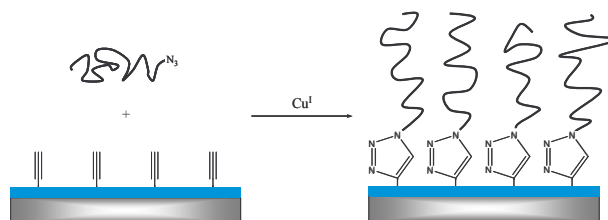
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### Abstract

Grafting of tailored macromolecular architectures is a convenient method widely developed in many industrial processes and fundamental studies to modify and control surface properties.<sup>1</sup> However, such strategies are generally only applicable to a narrow range of brush/substrate combinations and the functionalities eventually carried by the polymer backbone can alter the efficiency of the grafting process. Therefore, the development of new "grafting to" procedures able to be applied to a wide range of (functionalized) polymer brushes and substrates using a single robust and tunable tethering strategy is an exciting challenge.

In this scope, we developed a versatile and tunable "grafting to" approach based on the copper(I)-mediated Huisgen 1,3-dipolar cycloaddition of an azide (R-N<sub>3</sub>) and an alkyne (R-C≡CH),<sup>2</sup> an improved chemical pathway initially developed by Sharpless et al.<sup>3</sup> widely applied to the fields of polymer and materials sciences.<sup>4,5</sup> This grafting process allows for an irreversible tethering of polymer brushes as the resulting 1,4-disubstituted 1,2,3-triazole ring is thermally stable and relatively inert to hydrolysis, oxidation, and reduction. Therefore, a wide range of polymer brushes could be grafted to alkyne functionalized substrates obtained by the deposition of either a self-assembled monolayer of a monochlorosilane or a reactive pseudo-brush underlayer. Several experimental parameters were studied in order to tune the grafting process and the characteristics of the resulting brushes, i.e. reaction time (6-72h), polymer chemical nature (PS, PMMA and PEO), polymer weight fraction in the grafting solution (0.5-50 wt%) and polymerization degree of the chains (5000-50,000 g/mol). The thickness, grafting density, surface properties and morphology of the resulting brushes were mainly investigated by ellipsometry, scanning probe microscopy and water contact angle measurements.



**Scheme 1.** Click chemistry grafting of polymer brushes to alkyne functionalized substrates.

<sup>1</sup> Advincula, R. C., Brittain, W. J., Caster, K. C., Rühle, J. in *Polymer Brushes: Synthesis, Characterization and Applications* Wiley-VCH, Weinheim, **2004**.

<sup>2</sup> Ostaci, R.-V., Damiron, D., Capponi, S., Vignaud, G., Leger, L., Grohens, Y., Drockenmuller E. *Langmuir* **2008**, *24*, 2732.

<sup>3</sup> Kolb, H. C., Finn, M. G., Sharpless, K. B. *Angew. Chem. Int. Ed.* **2001**, *40*, 2004.

<sup>4</sup> Meldal M., Tornøe C. W. *Chem. Rev.* **2008**, *108*, 2952.

<sup>5</sup> Binder W.H., Sachsenhofer R. *Macromol. Rapid Commun.* **2008**, *29*, 952.

## Click Chemistry: Towards new Graft PCL-based copolymers

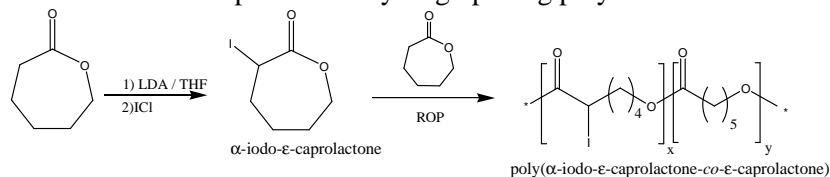
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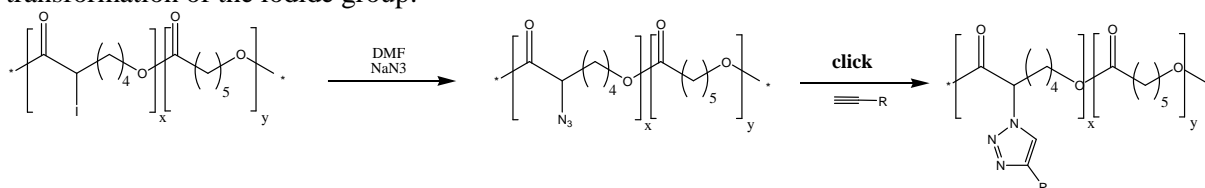
### Abstract

Biodegradable polymers are generally considered to be well-suited for applications as polymer-based biomaterials in biomedical and pharmaceutical fields for temporary applications.<sup>1</sup> Among all of them, aliphatic polyesters, such as poly(glycolide), poly(lactide), poly( $\epsilon$ -caprolactone) and their copolymers have a leading position as their hydrolytic and/or enzymatic degradation products are ultimately metabolized in most cases. While these polyesters are currently used in numerous biomaterial applications, they are limited in scope due to the absence of functionality on the polymer backbone. Pendent functionalization of aliphatic polyesters can be achieved by (co)polymerization of functionalized lactones, post-polymerization reaction, or both. With the emergence of new techniques such as controlled radical polymerization or click chemistry reactions, the combination of the two approaches is of particular interest. Aliphatic polyesters with pendent halogen or propargyl groups prepared by copolymerization of functionalized lactones are of particular interest. They give multiple possibilities for post-polymerization modification and grafting of functional units in the polyester backbone.

We have recently reported the synthesis of a new iodinated lactone,  $\alpha$ -iodo- $\epsilon$ -caprolactone and the polymerization of this functional caprolactone by ring opening polymerization.<sup>2</sup>



The iodinated poly( $\epsilon$ -caprolactone)s open the way to new functional polyesters by straightforward transformation of the iodide group.<sup>3</sup>



This contribution aims at reporting the synthesis of grafted PCL by click chemistry reaction using functional polyesters as polymeric substrate to obtain new macromolecular prodrugs.

<sup>1</sup> M. Vert, J. Feijen, A. C. Albertsson, G. Scott, E. Chiellini, "Biodegradable Polymers and Plastics", Royal Society of Chemistry, London **1992**.

<sup>2</sup> S. El Habnoui, V. Darcos, J. Coudane, *Macromol. Rapid Commun.* **2009**, *30*, 165.

<sup>3</sup> S. El Habnoui, V. Darcos, J. Coudane, *submitted*.

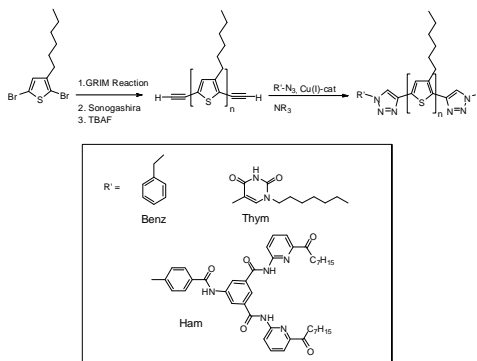
## AZIDE/ALKYNE-"CLICK" REACTION ON POLY(3-HEXYL)THIOPHENE AND CHARACTERIZATION WITH ESI-TOF AND MALDI-TOF MASS SPECTROSCOPY

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### Abstract

The aspect of multiple hydrogen bonding units has been receiving increased attention for application in supramolecular polymers. We are reporting on the preparation of hydrogen-bonded  $\pi$ -conjugated polymers from terminal alkyne modified poly(3-hexylthiophene) P3HT and azide functionalized hydrogen-bonding moieties via copper-catalyzed Huisgen dipolar 1,3-cycloaddition. Two different hydrogen-bonding systems bearing a thymine residue (**Thym**) and the Hamilton receptor consisting of a hexapolar hydrogen bonding moiety (**Ham**)<sup>1,2</sup> have been affixed to the chain end of the P3HT-polymers (Scheme 1).



Scheme 1

To this endeavour a bivalently functionalized poly(3-hexylthiophene) was synthesized either via a modified *GRIM- Grignard Metathesis polymerization*<sup>3</sup> using an alkynyl Grignard quencher or by introducing terminal alkynyl end groups via *Sonogashira-reactions* in a second step. Pure regioregular HT (*head-to-tail*)- poly(3-hexylthiophene)s were synthesized in a chain-growth mechanism based on 2,5-dibromo-3-hexylthiophene by addition of *tert*-butylmagnesiumbromide and Ni(dppp)Cl<sub>2</sub>. The reaction mixture resulted in the formation of a living P3HT effectively end-capped by a highly active Ni(0) group. Mono- as well as bicapped species were observed via ESI-TOF and MALDI-TOF upon addition of 100 mol% of ethynylmagnesiumbromide quencher. Additionally mono-acetylene-capped P3HT was obtained with 50 mol% of quencher, but a polymer devoid of acetylene-endgroups when using a concentration of 20 mol% quencher. Subsequently a copper-catalyzed "click" reaction was conducted in order to affix the H-bonding units onto the alkynyl telechelic poly(3-hexylthiophene), investigating different copper(I) species and bases such as tris-triazolyl ligands (tris(benzyltriazolylmethyl)amine TBTA). All end group modifications were proven by *matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS)* and *electrospray ionisation time-of-flight mass spectrometry (ESI-TOF MS)* coupled to LC- or SEC-methods.

<sup>1</sup> Chang, S. K.; Hamilton, A. D., Molecular recognition of biologically interesting substrates: synthesis of an artificial receptor for barbiturates employing six hydrogen bonds. *J. Am. Chem. Soc.* **1988**, 110, (4), 1318-1319.

<sup>2</sup> Binder, W. H.; Zirbs, R., Supramolecular Polymers and Networks with Hydrogen Bonds in the Main- and Side-Chain. *Adv. Polym. Sci.* **2007**, 207.

<sup>3</sup> Jeffries-El, M.; Sauve, G.; McCullough, R. D., Facile Synthesis of End-Functionalized Regioregular Poly(3-alkylthiophene)s via Modified Grignard Metathesis Reaction. *Macromolecules* **2005**, 38, (25), 10346-10352.

## FLUORESCENT CLICK-FUNCTIONALIZED Fe<sub>3</sub>O<sub>4</sub> MAGNETIC NANOPARTICLES

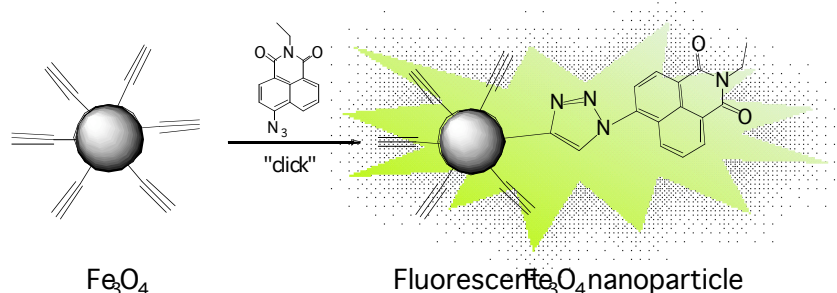
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<sup>1</sup>*Makromolekulare Chemie II, Universität Bayreuth, 95440 Bayreuth, Germany,  
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### Abstract

We report the reaction of click-functionalized Fe<sub>3</sub>O<sub>4</sub> nanoparticles (NPs) with a fluorogenic compound based on azido-1,8-naphthalimide<sup>1</sup> as a technique to visualize the click-modification of Fe<sub>3</sub>O<sub>4</sub> magnetic NPs. The Huisgen [2+3] cycloaddition was used to attach clickable 4-Azido-*N*-ethyl-1,8-naphthalimide (Scheme 1) to alkyne-modified Fe<sub>3</sub>O<sub>4</sub> NPs. The azide/alkyne click-reaction includes often quantitative yields, a high tolerance of functional groups, an insensitivity of the reaction to solvents, irrespective of their protic/aprotic or polar/non-polar character.<sup>2</sup> In this context, click-chemistry is an effective approach because 4-azido-*N*-ethyl-1,8-naphthalimide takes advantage of the electronic structure changes associated with the triazole ring formed in the Cu(I)-catalyzed azide-alkyne ligation reaction with alkyne Fe<sub>3</sub>O<sub>4</sub> NPs. Fluorescence spectroscopy and confocal fluorescence microscopy are explicit methods to prove the effective surface functionalization.

We demonstrate the synthetic strategy of alkyne-surface modified Fe<sub>3</sub>O<sub>4</sub> magnetic particles as well as the click-reaction with the fluorogenic compound. The general synthetic strategy is shown in Scheme 1.



Scheme 1. Fluorescent Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles via Huisgen [2+3] cycloaddition

<sup>1</sup> M. Sawa, T.-L. Hsu, T. Itoh, M. Sugiyama, S. R. Hanson, P. K. Vogt, C.-H. Wong, *PNAS* **2006**, 103, 33, 12371-12376.

<sup>2</sup> Binder, W. H.; Sachsenhofer, R. *Macromol. Rapid Commun.* **2007**, 28, 15–54.

## INFLUENCE OF TRIAZOLE-MOIETIES ON THE LIVING CATIONIC POLYMERIZATION OF ISOBUTYLENE (IB)

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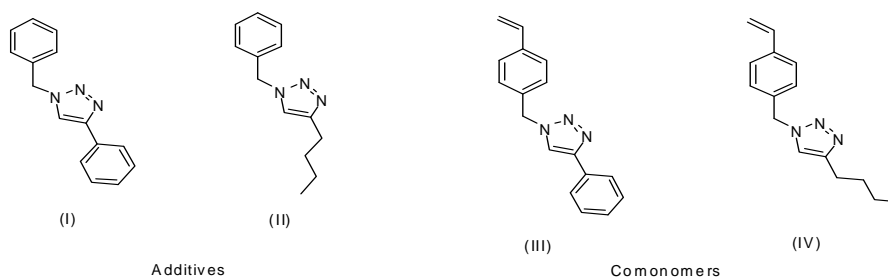
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### Abstract

Copolymers of isobutylene and functionalized styrenes prepared via quasiliving cationic polymerization are widely known in literature<sup>1, 2</sup>. One strategy to introduce functional moieties into polymers by post-functionalization of copolymerized precursors is the azide/alkyne-“click”-reaction<sup>3</sup>. Another strategy to generate copolymers is depicted in figure 1, using comonomers **III** and **IV**, containing the already preformed triazoles. To date no copolymerization of triazole-functionalized styrene monomers with isobutylene via carbocationic polymerization has been described.

We investigate the influence of additives and comonomers bearing triazole-moieties on the kinetics of the carbocationic homopolymerization of isobutylene and carbocationic copolymerization with the functionalized styrene comonomers (**III**), (**IV**).



**Figure.1** Structure of comonomers and additives bearing the triazol moieties

Styrene monomers **III** and **IV** and the nonpolymerizable additives **I** and **II** were synthesized and characterized by NMR-spectroscopy. Subsequently, they were copolymerized statistically with isobutylene in different amounts ranging from 1 - 7 mol %. The copolymerization kinetics of isobutylene and comonomers (**III**) and (**IV**) were monitored *via* in-situ-ATR-FTIR-spectroscopy<sup>1</sup> in order to investigate the influence of the triazole-moiety (**III**), (**IV**). Analogously the isobutylene was homopolymerized in the presence of the additives (**I**) and (**II**) in order to compare the influence on the copolymerization kinetics.

As compared to the  $k_{app}$  for the homopolymerization of pure isobutylene ( $7 \times 10^{-3} \text{ s}^{-1}$ ) the  $k_{app}$  for 1 mol% of **I** is  $6 \times 10^{-2} \text{ s}^{-1}$  and  $k_{app}$  for 7 mol% of **I** is  $3 \times 10^{-2} \text{ s}^{-1}$ . The  $k_{app}$  of the copolymerization of **III** is also significantly enhanced as  $k_{app} = 6 \times 10^{-2} \text{ s}^{-1}$  (1 mol % of **III**) and  $1 \times 10^{-2} \text{ s}^{-1}$  (7 mol % of **III**), which is comparable to the  $k_{app}$  of homopolymerization of isobutylene with additive (**I**).

Hence, it can be concluded that the triazole-moiety has a strong influence on the rate of polymerization.

<sup>1</sup> Storey, R. F.; Thomas, Q. A., Quasi-Living Cationic Polymerization of Styrene and Isobutylene: Measurement of Run Number and Calculation of Apparent Rate Constant of Ionization by  $\text{TiCl}_4$ . *Macromolecules* **2003**, 36, (14), 5065-5071.

<sup>2</sup> Puskas, J. E.; Chan, P.; McAuley, K. B.; Kaszas, G.; Shaikh, S., Real-Time FTIR Monitoring of the Carbocationic Copolymerization of Isobutylene with Styrene. *Macromol. Symp.* **2006**, 240, (1), 18-22.

<sup>3</sup> Tilliet, M.; Lundgren, S.; Moberg, C.; Levacher, V., Polymer-Bound Pyridine-Bis(oxazoline). Preparation through Click Chemistry and Evaluation in Asymmetric Catalysis. *Advanced Synthesis & Catalysis* **2007**, 349, (13), 2079-2084.

## "CLICKABLE" ORGANOPHILIC MONTMORILLONITE IN POLYMER/CLAY NANOCOMPOSITES

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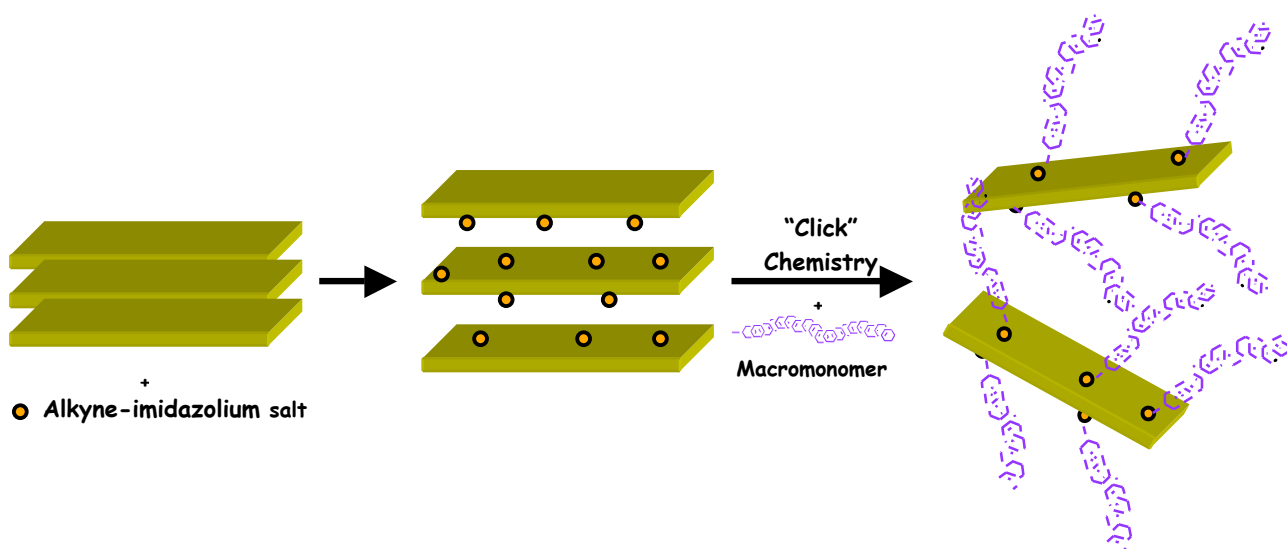
It is a well known issue that the Huisgen 1,3-dipolar cycloaddition reaction between terminal azides and alkynes, catalyzed by Cu(I) complexes, is one of most efficient "click" reactions because of the short reaction time, its high yield, the mild reaction conditions, and a high tolerance toward other functional groups<sup>1</sup>. This "click" reaction has been applied in many chemistry fields, for example for the surface modification in macromolecular engineering, for the nanoparticle and carbon nanotubes functionalization and in nanostructured semiconductors. However, only a limited number of works has been reported on polymer/clay nanocomposites<sup>2</sup>.

Regarding the clay, the limited thermal stability of cations intercalated into smectites minerals and the processing instability of some polymers in the present of nanodispersed montmorillonites (MMT) motivated the development of improved organophilic treatments for layered silicates<sup>3</sup>. Our efforts to address this issue has been focused on the use of new thermally stable imidazolium-treated "clickable" silicates for the preparation of nanocomposites.

In this work a imidazolium salt derivative was prepared with a propargyl chain attached to imidazolium through one of the nitrogen atoms and then characterized by FTIR, RAMAN and <sup>1</sup>H-NMR. This imidazolium salt was used to prepare the corresponding organophilic MMT and then characterized by TEM, TGA and RX.

We report here that the use of 1-propargyl-2,3-dimethylimidazolium salts to replace the cations in MMT gives organophilic MMT with an improvement of the thermal stability as compared to classical organophilic MMT, with an increase in the *d* spacing between layers. A new class of "organophilic MMT-click" components is presented and its use to established with optimum compatibility between the clay and the polymer.

After an approach it is possible to asses that the use of "click" chemistry would be an ideal modular methodology for the intercalation of macromonomers with a well-defined structures into the galleries of the silicate, and subsequent anchoring to the organophilic MMT for the preparation of stable nanocomposites.



<sup>1</sup> Kolb H. C., Finn M. G., Sharpless K. B. *Angew. Chem., Int. Ed.*, **2001**, 40 (11), 2004-2021

<sup>2</sup> Tasdelen M. A., Camp W. C., Goethals E, Dubois P., Du Prez F., Yagci Y. *Macromolecules* **2008**, 41, 6035-6040

<sup>3</sup> Gilman J. W., Awad W. H., Davis R.D., Shields J., Harris Jr R. H., Davis C., Morgan A. B., Sutto T. E., Callahan J., Trulove P. C., DeLong H. C. *Chem. Mater.* **2002**, 14, 3776-3785

## Ultrafast Click Conjugations for Ambient Temperature Macromolecular Engineering

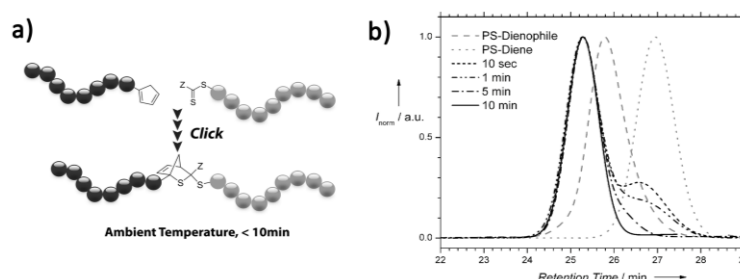
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### Abstract

The union of the *click* philosophy and synthetic polymer science has given rise to a wide variety of novel functional materials in recent years.<sup>1</sup> As synthetic requirements for obtaining such materials becomes more and more demanding, the continued development of highly efficient and orthogonal conjugation reactions beyond the copper (I) catalyzed Azide-Alkyne Cycloaddition (CuAAC) is of high importance. Our contribution to this field has been focused on the RAFT-HDA concept. This technology involves the sequential usage of the dithioester end-group inherent to polymers prepared via RAFT polymerization for mediating controlled polymerization and also as a reactive dienophile in a hetero Diels-Alder cycloaddition. Thus far, this technology has successfully and efficiently been applied to the construction of block copolymers,<sup>2</sup> star polymers<sup>3</sup> and surface functionalization of polymeric microspheres.<sup>4</sup> Each of these examples proves to be very comparable to the CuAAC in terms of both reaction conditions and efficiency. However, in aim of a conjugation system that more closely resembles the *clicking* together of *lego* building blocks, we have developed an ultrafast *click* strategy that may be performed under ambient temperature and atmosphere and without catalyst.<sup>5</sup>



**Figure 1.** a) Ultrafast click conjugation of macromolecular building blocks via RAFT-HDA chemistry; and b) Kinetic analysis of block copolymer formation via Size Exclusion Chromatography.

Polymers prepared via Atom Transfer Radical Polymerization (ATRP) were equipped with a cyclopentadiene (Cp) end-group via a simple nucleophilic substitution of the polymer's terminal bromide. The resulting Cp-functionalized polymers could then be *clicked* to polymers prepared via the RAFT process by simply dissolving both polymers in a common chloroform solution (Figure 1a). Inspection of Figure 1b clearly shows that the majority of the block copolymer structure is formed within the first 10 seconds of reaction. It is therefore apparent that this novel variant of RAFT-HDA chemistry is highly efficient. The very benign reaction conditions and the speed of the conjugation make such a synthetic tool very appealing to the construction of a wide variety of sensitive, bio-relevant hybrid materials.

<sup>1</sup> Binder, W. H.; Sachsenhofer, R. *Macromol. Rapid Commun.* **2008**, *29*, 952.

<sup>2</sup> Sinnwell, S.; Inglis, A. J.; Davis, T. P.; Stenzel, M. H.; Barner-Kowollik, C. *Chem. Commun.* **2008**, 2052.

<sup>3</sup> a) Inglis, A. J.; Sinnwell, S.; Davis, T. P.; Barner-Kowollik, C.; Stenzel, M. H.; *Macromolecules*, **2008**, *41*, 4120;

<sup>4</sup> Nebani, L.; Sinnwell, S.; Inglis, A. J.; Stenzel, M. H.; Barner-Kowollik, C.; Barner, L. *Macromol. Rapid Commun.* **2008**, *29*, 1431.

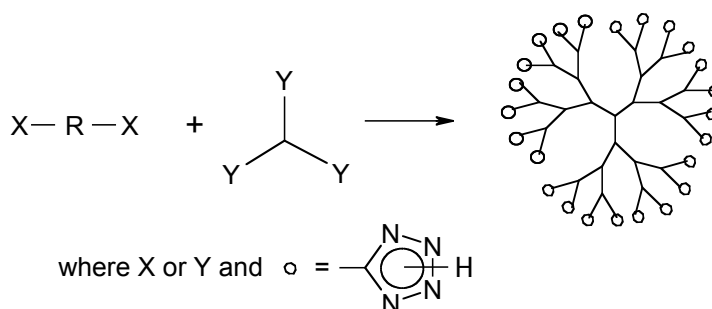
<sup>5</sup> Inglis, A. J.; Sinnwell, S.; Stenzel, M. H.; Barner-Kowollik, C. *Angew. Chem. Int. Ed.* **2009**, *48*, 2411.

## HYPERBRANCHED TETRAZOLE-CONTAINING POLYMERS

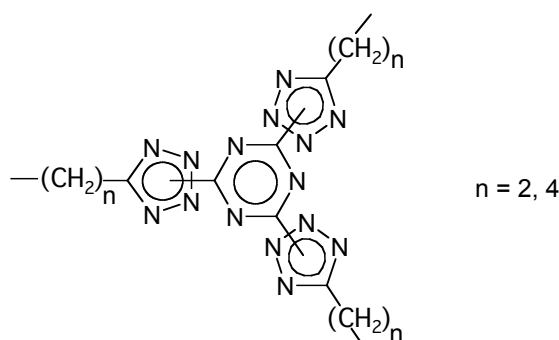
VALERY N. KIZHNYAEV, FEDOR A. POKATILOV, LEONTY I. VERESHCHAGIN,  
 ALEXANDER I. SMIRNOV

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 st. Karla Marksa, 1, Irkutsk, 664003, Russia - [kizhnyaev@chem.isu.ru](mailto:kizhnyaev@chem.isu.ru)*

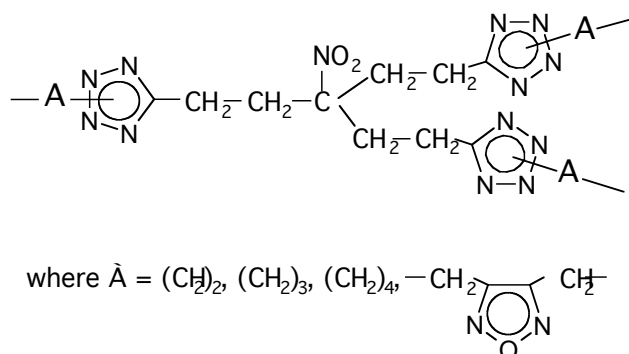
Uncondensed bis- and tris-tetrazoles with nonsubstituted N-H function can serve as monomers for the synthesis of hyperbranched polymeric acids.



In case of bis-tetrazoles as three-functional comonomer cyanuric chloride was used. In that case the polymer had a branched fragment:



When applying bis-tetrazoles as difunctional comonomer dihalide of different structures were used. Hyperbranched polymers with fragments were synthesised:



The polymers obtained, represent one more type of nitrogen high energetic polymeric materials.

## Au NANO-PARTICLES AND NANO-LAYERS GRAFTED ON PLASMA TREATED POLYETHYLENE

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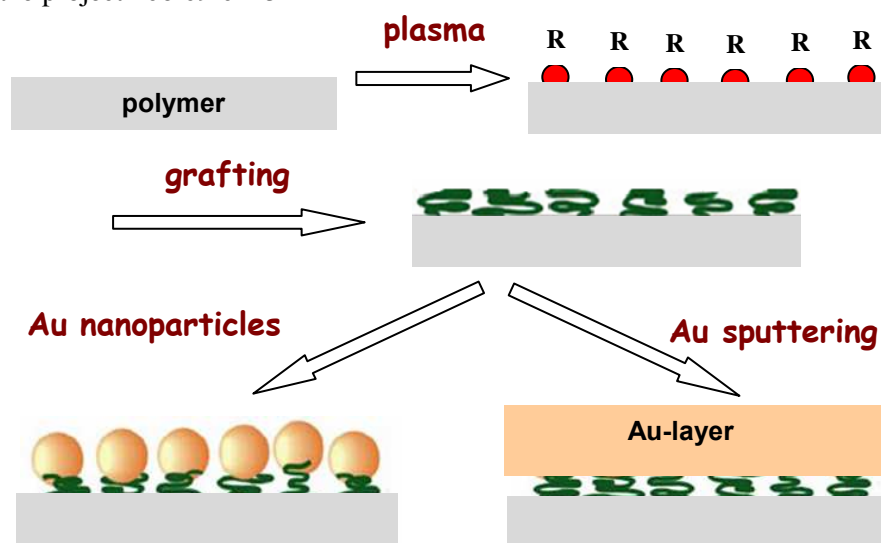
<sup>4</sup>New Technologies-Research Centre in Westbohemian Region, University of West Bohemia, Plzen, Czech Republic

### Abstract

The systems combining metals with polymers are attractive for many applications, especially in microelectronics.<sup>1,2</sup> Surface of polyethylene (PE) was treated with Ar plasma. Activated surface was grafted from methanol solution of 1,2-ethanedithiol. Then the sample was immersed (i) into freshly prepared colloid solution of Au nano-particles and (ii) 50 nm thick gold nano-layer was sputtered on the sample. Properties of the modified PE were studied using XPS, AFM, EPR, RBS methods and nanoindentation. It was shown that the plasma treatment results in degradation of polymer chain, creation of free radicals and conjugated double bonds. After grafting with 1,2-ethanedithiol the concentration of free radicals declines but the concentration of double bonds remains unchanged. Plasma treatment changes PE surface morphology and increases surface roughness too. Another significant change in surface morphology and roughness was observed after deposition of Au nano-particles. The presence of Au on the sample surface after the coating with Au nano-particles was proved by XPS and RBS methods. Nanoindentation measurements shown that the grafting of plasma activated PE surface with dithiol increases adhesion of sputtered Au nano-layer.

### Acknowledgements

This work was supported by the Ministry of Education of the Czech Republic under programs 6046137302 and LC 06041, GAAS CR under the projects KAN 400480701 and 200100801 and GACR under the project 106/09/0125.



<sup>1</sup> Z. Li, A. Friedrich, A. Taubert, J. Mater. Chem. 18, 1008 (2008).

<sup>2</sup> V. Kotál, V. Švorčík, P. Slepíčka, O. Bláhová, P. Šutta, V. Hnatowicz, Plasma Proc. Polym. 4, 69 (2007).

## FUNCTIONAL COPOLYMERS OF N-VINYL-2-PYRROLIDONE WITH METHACRYLOIL CHLORIDE –SYNTHESIS, DESIGN AND IMMOBILIZATION OF BIOPREPARATES

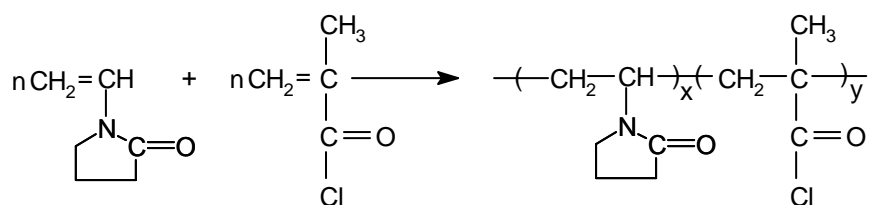
VITAN B. KONSULOV<sup>1</sup>, ANASTASIA A. LYAPOVA<sup>1</sup>, ZOYA S. GROZEVA<sup>1</sup>, PETR SACHA<sup>2</sup>

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<sup>2</sup>Tomas Bata University in Zlin, nam. JGM 5555,76061 Zlin, Czech Republic

### Abstract

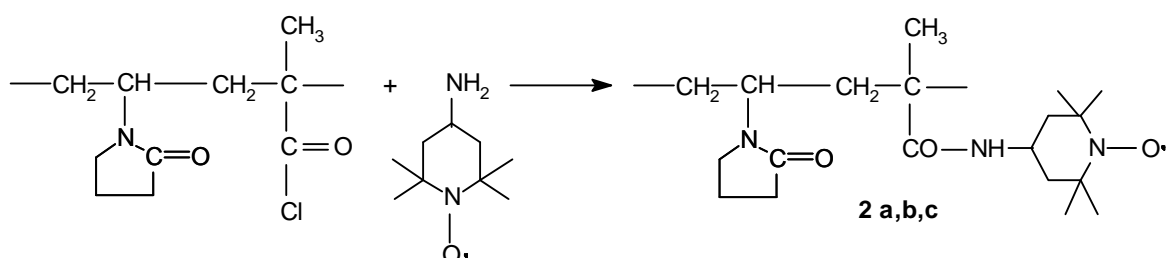
The free radical copolymerization of N-vinyl-2-pyrrolidone (VP) with methacryloilchloride (MC) was carried in the presence of 2,2'-azo-bisisobutyronitrile as initiator in tetrahydrofuran (THF), or 1,2-dichloroethane (DCE) solutions at 60°C:



### 1 a-f

The structure of the resulting reactive copolymers poly(N-vinyl-2-pyrrolidone-co-methacryloilchloride) was proved by elemental analysis (N and Cl content), NMR and IR-spectroscopy: 1668 cm<sup>-1</sup> (νC=O, amide I) for VP units, and 1375, 1460 cm<sup>-1</sup> (δs,as CH<sub>3</sub>) for MC units. Copolymer samples **1 a-f** were obtained by copolymerization of mixtures of VP (M<sub>1</sub>) and MC (molar ratios-from 1:9 to 9:1) to approximately 10 % conversion. The results were used to calculate the corresponding copolymerization reactivity ratios by both the Kelen-Tüdös (KT-komputer programme) method, and are as follows: r<sub>1</sub>=0.17, r<sub>2</sub>=0.14 in DCE, and r<sub>1</sub>=0.07, r<sub>2</sub>=0.22 in THF. The influence of the nature of the solvents is proved.

By the polymeranalogous reaction of reactive copolymers poly(VP-co-MC) with the adenine, sulfatiozole, antranilic acid and holinchloride were immobilized. New copolymers of VP containing nitroxide radicals were prepared by the reaction reactive copolymer **1** with 4-amino-2,2,6,6-tetramethylpiperidine-1-oxyle (A-TEMPO):



The structure of the new polynitroxide copolymer **2** was investigated by EPR and FT-IR spectroscopy. The typical triplet signals in the EPR-spectra, also bands about 1340, 1197 and 975 cm<sup>-1</sup> (stretching NO) in IR spectra of obtained copolymers **2 a,b,c**, containing TEMPO is a proof for stable piperidiloxide radicals in the macromolecules.

**Keywords:** copolymerization, N-Vinyl-2-pyrrolidone, reactivity ratios, nitroxide radicals, TEMPO.

## POLIMERIZATION BY CLICK REACTION FOR THE DESIGN OF DENDRIMERS-LIKE POLYMERS.

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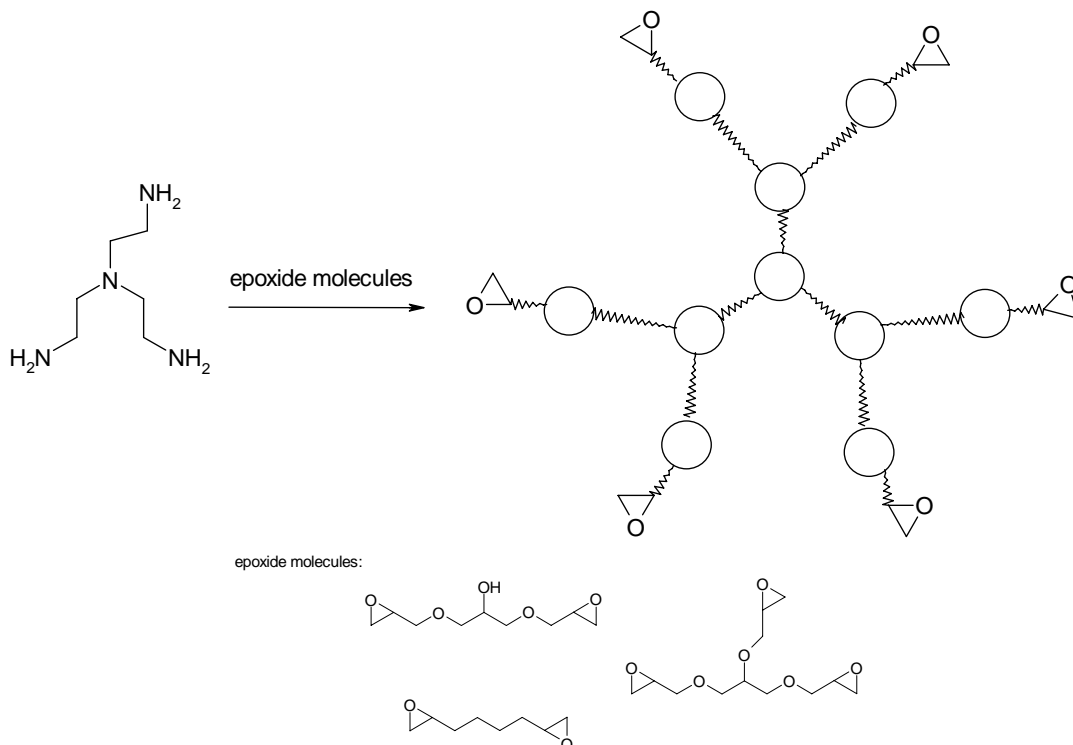
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### Abstract

Enzyme immobilization is often required for most industrial applications. Epoxy-activated supports are almost-ideal matrixes to perform a very easy immobilization of proteins on both laboratory and industrial scale. Epoxy groups are able to react with different groups of the protein that are very abundant on the protein surface (such as amino, thiol, phenolic and imidazole).

Following Sharpless's lead about "Click chemistry" we have created dendrimers-like polymers structures through the reaction between small molecules with oxirane groups and *tris*(aminoethyl amine) as core. This methodology allows obtaining epoxy-activated supports for enzyme immobilization. The synthesis process is not sensitive to oxygen neither water, the reactants are quite available and the final materials can be isolated easily from the reaction medium by filtration.

The obtained materials were characterized by <sup>1</sup>H-RMN, <sup>13</sup>C-RMN solid state and IR spectroscopy and those were analyzed by differential scanning calorimetry (DSC), thermogravimetry (TGA) and nitrogen adsorption.



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