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REVIEW

Dye-functionalized polymers via ring opening metathesis polymerization: principal routes and applications

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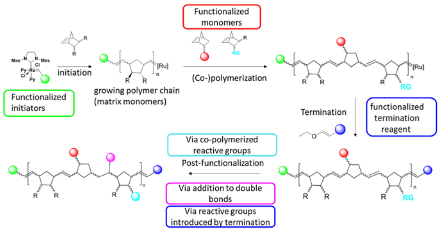
Abstract Herein, highlights from the recent literature regarding functional dye-polymer conjugates obtained by ring opening metathesis polymerization (ROMP) are presented and the different approaches to incorporate dyes during the initiation, propagation, and termination step in ROMP are discussed. Applications in the field of chemical sensors, bioimaging, electroactive materials, self-assembly, photochromic and photoreactive materials are used to illustrate the versatility of ROMP as a technique to prepare complex functional materials.

Graphical abstract



Keywords Norbornenes · ROMP · Optical properties · Material science · Dyes · Sensors

Introduction

Dye-functionalized polymers are useful in a plenitude of current applications in research and technology. Firstly, the covalent attachment of dye molecules to the polymer main chain prevents leakage of the dye molecules reducing aggregation and thus leading to more homogeneously distributed chromophores within the matrix polymer. This consequently leads to functional polymeric materials for different optical applications. In addition, by attaching a dye to an amphiphilic block copolymer and using their self-assembly and aggregation behavior, hydrophobic and non-water-soluble materials can be introduced in an aqueous environment which enables dye-polymer conjugates to be used in labeling experiments, ranging from cell staining to in vivo applications.

Furthermore, additional functionalities such as biomarkers, photoreactive groups, nanoparticles, or functional groups, which allow an interaction with surfaces, can be incorporated in dye-polymer conjugates. In addition to the principal question of the reliable attachment of the dye to the polymer, the location of the dye molecule on the polymer chain is of almost the same importance. Since an ideal polymerization technique for the preparation of such multifunctional materials requires precise control of the incorporation of two or more monomers with different functionalities, ring-opening metathesis polymerization (ROMP) has received wide reception for the preparation of such specialty polymers. The initiators for ROMP have evolved in a way which enables living polymerization (characterized by complete and rapid initiation, irreversible propagation steps, and the absence of undesired chain termination or chain transfer reactions) allowing the preparation of polymers with a narrow molecular weight distribution, and, even more importantly, the preparation of

Dedicated to our mentor and head of ICTM, Prof. Dr. Franz Stelzer.

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block copolymers. This, in combination with a high functional group tolerance and mild reaction conditions makes ROMP a very well suited method for the preparation of functional materials and specialty polymers [1–5].

This concept paper is aimed at giving an overview of the different strategies to obtain dye-functionalized ROMP polymers and discussing their advantages and disadvantages based on selected examples for synthesis and applications found in literature.

Approaches towards defined dye-functionalization of ROMP-polymers

There are several strategies to introduce functionalities such as dyes into ROMP polymers (see Fig. 1). Firstly, the carbenoid ligand of the initiator remains in the polymer chain so that suitably derivatized initiators can be used to label a polymer chain at its beginning with a dye molecule. Secondly, in the most common approach, monomers can be equipped with dye molecules and (co)polymerized to defined dye-functionalized (co)polymers. Thirdly, the termination reagents can be derivatized so that one dye molecule can be attached to the end of the polymer chain. Alternatively, reactive groups can be incorporated in the initiation, propagation, and termination steps and the dye molecule is subsequently introduced in a post-polymerization functionalization approach. In addition to these methods, the double bonds in the polymer backbone are also available for post-polymerization functionalization.

With these various methods at hand, ROMP allows for precise placement of dye molecules within polymer chains and materials. Table 1 gives an overview of different dye categories for being incorporated in ROMP polymers using the aforementioned techniques.

It is also worth mentioning that ROMP can be used to prepare conjugated polymers which can be considered as dye molecules themselves as covered in a recent review by Bunz et al. [6]. Another interesting class of materials are liquid crystalline ROMP polymers containing large polyaromatic and rigid moieties [7]. However, this work aims at giving examples on how the incorporation of functionalized dyes into ROMP polymers can be utilized to prepare functional materials which is why these topics will not be included in this work. Additionally, we focus herein on the scope and limitations of ROMP polymers applied in chemosensors, bioimaging, organic electronics, self-assembled structures, and photoreactive materials.

Functionalization by dye-modified initiators

The carbenoid ligand in the transition metal carbene initiators (typically a benzylidene or indenylidene group) remains at the beginning of the polymer chain. Therefore, attaching dyes to this ligand has the advantage that all

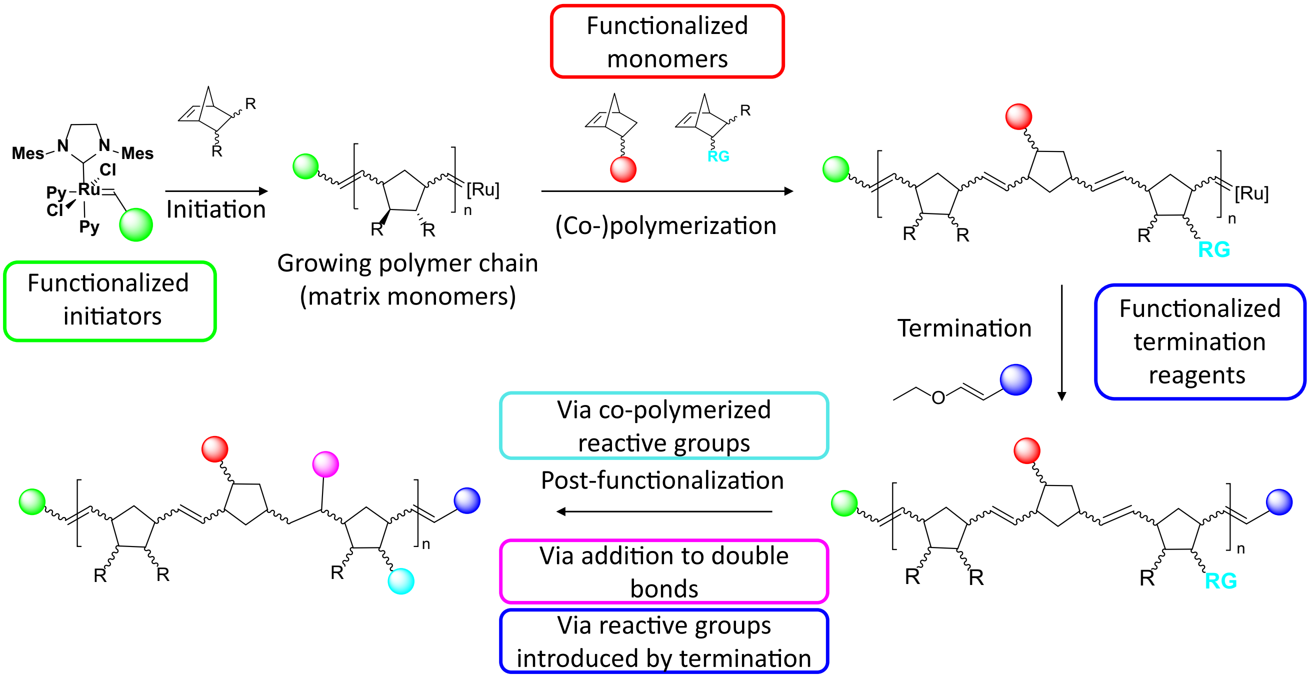


Fig. 1 Schematic representation of possible ways to introduce dye-functionalities into a ROMP polymer: via initiation (*green spheres*), functionalized monomers (*red spheres*) or reactive groups (RG), termination (*blue spheres*) or post-functionalization reactions (*pink spheres*)

Table 1 Different routes to dye-functionalized polymers and used dye categories

Dye category	Homopolymers	Random copolymers	Block copolymers	Initiator	Termination reagent	Reactive groups	Post-functionalization
(Hetero)acenes	Anthracene [15–17], pentacene [18], tetracene [18]	Anthracene [15, 17], pyrene [19], benzothienobenzothiophene [20]	–	–	Anthracene [74]	–	Fluorene [90]
(Hetero)cycles	Perylene bisimides [21–24], hexabenzocoronene [25–27], quinolone [26], pyrene [29]	Phenanthroimidazole [30, 31] perylene bisimides [21], quinizarine [32], phenoxynaphthacene [33]	Perylene bisimides [21]	Phenanthroimidazole [11], perylene bisimides [8], pyrene [9]	Coumarin [79]	Benzoxazole [81]	Benzoxazole [76, 90]^a
Triphenylmethane dyes	(Dichloro)fluorescein [40], eosin [40]	Eosin [41]	Oregon Green 488 [42], rhodamin B [43], rhodamin [44], fluorescein [44], eosin [45–47]	Fluorescein [10]	Rhodamin, [10, 92] fluorescein, [10, 92]	–	Rhodamin B^a [77], rhodamin 123^a [78], fluorescein^a [79]
Azo dyes	[48–52]	[48]	–	–	–	–	–
Polymethine dyes	Spiropyrans [53–55]^b, spirooxazines [56]^b	Spiropyrans [53, 57]^b		–	–	Indocyanine green [84, 88, 89]	Indocyanine green [85]
Transition metal coordination compounds	Al [58, 59], Ru [64], Fe [52, 60], Ir [67]	Al [58], Pt [70], Zn [61, 62], Ir [68, 69], Eu [66]	Ru [64, 65], Pt [70–72], Ir [68], Zn [63], Eu [66]	Tb [12]	–	–	Eu [91]
Conjugated oligomers and electroactive materials	Oligo-EDOT [34], oligo-PPV [35], fluorene-carbazole trimers [36], oligothiophene [37], triphenylamine [38, 39]	Oligo-EDOT [34]	–	–	Oligothiophene [75]	2PA dyes [82]	Oligo-PPV [35]^a

[a] Post-functionalization of semi-telechelic polymers with reactive end groups

[b] Reversible photoreaction to merocyanines

polymer chains are labeled so that polymerization kinetics and dye aggregation do not influence the dye content of the macromolecule. However, for certain applications, a higher dye content is required which cannot be achieved by this method (only one dye molecule per chain can be incorporated). Furthermore, for this functionalization technique, new initiators need to be synthesized for each dye class, which can be more challenging than monomer synthesis in some cases. A typical method for this is carbene exchange of a ROMP initiator with a suitable precursor. In addition, there is a potential interference between the initiator and the pending dye due to sterical hindrance or functional groups of the dye which could alter the polymerization kinetics, especially of the initiation step. Consequently, this route has not been used very often and only relatively innocuous dyes like perylenebisimides [8], pyrene [9], or phenanthroimidazole [11] have been employed whereas fluorescein [10] could be only used after protecting the O–H functionalities, see Fig. 2.

Alternatively, a labeled ROMP initiator can be prepared in situ by carbene exchange with a terminal olefin, subsequently followed by polymerization, which has been shown for a terbium coordination compound [12].

Functionalization by dye-substituted monomers

Conceptually, the (co)polymerization of a suitably derivatized monomer is the most straightforward method to obtain a highly functionalized polymer. [2.2.1]Bicyclohept-5-ene-derivatives (norbornenes) are the most common monomers in ROMP, as a huge variety of different monomers can be produced by a [4+2]-cycloaddition (Diels–Alder reaction) of a dienophile (electron-deficient alkene) and a conjugated diene, in most cases cyclopentadiene or furan.

Alternatively, large and complex functionalities can be easily introduced by esterification or etherification reactions. E.g., for the anchoring of a dye via an ester group, norbornoyl chloride is usually prepared in situ from acryloyl chloride and cyclopentadiene, followed by reaction with the corresponding alcohol. Depending on the environment where the polymer will be applied in, esters as anchor groups might be subject to hydrolysis and could be replaced by ethers, amides, imides or aliphatic chains. However, one should consider that anchor groups have an influence on the polymerization rate [13, 14] and monomers which are sterically unhindered bear the inherent risk of backbiting via a cross-metathesis mechanism leading to ill-defined polymeric products. In addition to the nature of the anchoring groups, the polymerization rate constants also depend on the stereochemistry on the norbornene and thus on the configuration of the substituents in 2- and 3-position (*exo* or *endo*). To minimize these effects, bi-functional norbornene derivatives are often applied. These are typically prepared by [4+2]-cycloaddition of cyclopentadiene to *trans*-alkenes such as fumaric acid leaving a racemate of *endo*-, *exo*-substituted norbornenes. In contrast, mono-substituted alkenes lead to a mixture of *endo*- and *exo*-products with significant differences in their propagation rate. Nevertheless, the density of functional groups in the polymer can be additionally varied by changing between mono- and bi-functional norbornene derivatives. Another popular choice of monomer are norbornenes and 7-oxanorbornenes derived from maleimide and cyclopentadiene or furan, respectively. While, due to their easy synthetic availability, norbornenes are used in the majority of ROMP-related publications, other strained olefin monomers such as cyclobutene, cyclopentene, or cyclooctene [8] have been used for special applications such as the synthesis of highly regular LDPE.

The majority of dye-functionalized ROMP polymers has been obtained following a functional monomer approach (Table 1). A wide range of suitable monomers has been copolymerized comprising (hetero)polyaromatic compounds [15–33], and more sophisticated functionalities like conjugated oligomers [34–39], triphenylmethane [40–47], azo [48–52], or polymethine [53–57] dyes. Even transition metal coordination compounds of aluminum [58, 59], iron [60], zinc [61–63], ruthenium [64, 65], europium [66], iridium [67–69], and platinum [70–72] have been successfully incorporated into ROMP polymers.

Functionalization via the termination reagent

To terminate a ring-opening metathesis polymerization, the active carbenoid species residing on the polymer chain needs to be converted into a less reactive form to avoid backbiting and other cross-metathesis reactions [73]. One approach thereby is to directly incorporate dyes by cross-metathesis, either with dye-functionalized alkenes [10] or with dyes bearing acrylate or vinyl ether functionalities,

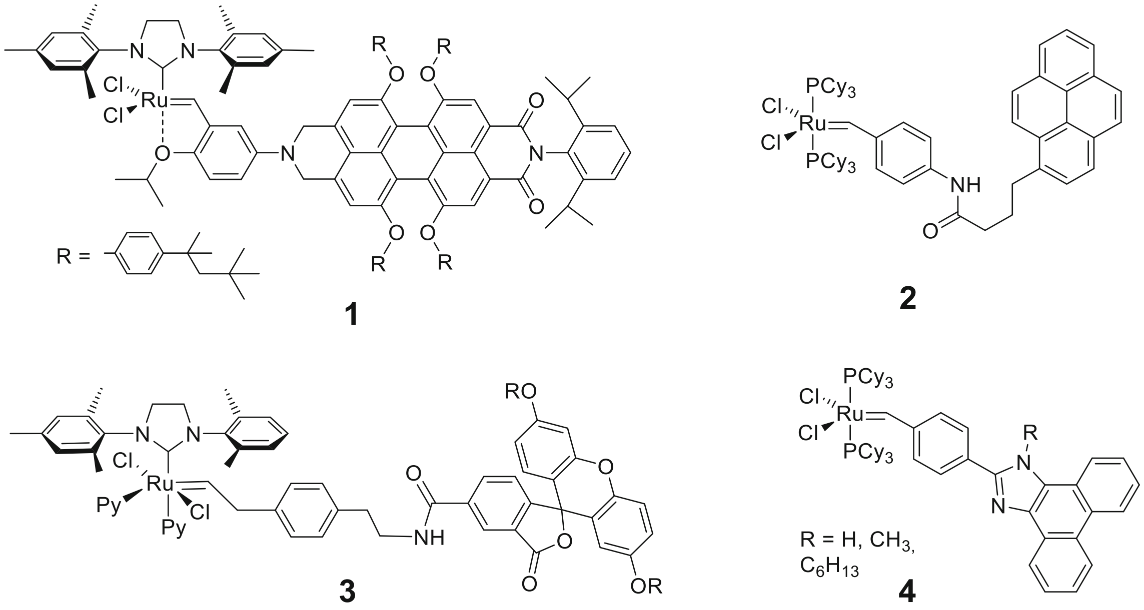


Fig. 2 Chemical structures of dye-functionalized initiators: perylene bisimides (**1**) [8], pyrene (**2**) [9], fluorescein (**3**) [10], and phenanthroimidazole (**4**) [11]

which convert the carbenoid species residing in a polymer chain into a less reactive, Fischer-type carbene. It should be noted that using dye-functionalized vinylether terminating agents results in quantitatively dye-labeled polymer chains; using acrylate-functionalized terminating reagents results in formation of a significant amount of methylene terminated polymer chains as side product [74]. Aldehydes react with Schrock-type (molybdenum carbene) initiators as well as tungsten or titanium-based initiators in a Wittig-type reaction and can be used as terminating reagents for these systems [35, 73, 75].

The synthesis of dye-functionalized termination reagents is, in most cases, as straightforward as for dye-functionalized monomers and initiator stability is obviously not an issue which is an advantage compared to functionalized initiators. While functional group placement is limited to one unit at the end of each polymer chain, this approach is complementary to the initiator route so that both ends can be labeled if desired. Alternatively, a reactive group such as activated esters, ketones, or azides can be introduced via the above-mentioned methods which can be then further used to attach dye molecules, an approach which has been quite frequently pursued [3, 76–79].

More detailed information on the introduction of reactive groups in the termination step can be found in recent reviews by Kilbinger [73] and Nomura [3].

However, only living polymer chains are labeled at the end which leads to some polymer chains being possibly unlabeled—those which terminated during the polymerization process due to backbiting, impurities in the monomer, or contaminants (e.g., oxygen) in the solvent.

Post-polymerization modification

With the increasing demand for multifunctional materials containing components which are even beyond the impressive substrate scope of ROMP initiators, post-polymerization functionalization has become increasingly attractive, also for polynorbornenes and other ROMP polymers. However, this more general method requires an efficient and chemoselective coordination or reaction step.

Frequently used reactive motifs for post-polymerization functionalization [80] are hydroxyl, amino, carboxylic acid, activated ester (such as succinimidyl or pentafluorophenyl esters), azide, alkyne, alkene, thiol, or maleimide groups.

While activated esters [10, 77, 81, 82] and maleimide functionalities can be straightforwardly (co)polymerized via ROMP, terminal alkynes would participate in a metathesis reaction and therefore need to be protected, typically by a trimethylsilyl group which can be conveniently cleaved after polymerization using tetrabutylammonium fluoride. Azides are also not compatible with ROMP but can be introduced after polymerization by nucleophilic substitution of pendant alkyl halogenide chains [83–85]. However, the triazolyl groups formed in copper catalyzed azide-alkyne click chemistry do not have a negative effect on ROMP [43, 86].

Another possibility is to introduce a derivatizable functionality by carbene exchange in direct precedence of polymerization, similar to the aforementioned in situ labeling of initiators. In most cases, protecting groups need to be applied to make sure the initiator does not change its reactivity [87]. Since this is no issue in the termination step, more functionalities can be introduced at this stage in an unprotected form.

Functionalization of double bonds in the poly(norbornene) backbone

In addition to derivatizable groups which may be introduced at any stage of the ROMP polymerization process, the double bonds of the polymer backbone can be used for introducing additional functionality, which was initially used for hydroxylation [84, 85, 88, 89], epoxidation [17], and sulfonation [17].

Exhaustive hydrogenation of polynorbornenes [8, 29] was mainly performed to improve oxidative stability of the now aliphatic materials. Taking place under relatively mild reaction conditions, radical thiol-ene [90] reactions have been recently used to attach dye molecules (fluorene and benzoxazole) directly to a polynorbornene backbone. In another novel approach, tetrazines were used to graft dipyridylpyridazine ligands in an inverse electron demand Diels–Alder reaction to a polydicyclopentadiene foam prepared by emulsion templating. Successful grafting of the ligands was proven by the formation of red phosphorescent europium complexes on the surface of the polymeric foams [91].

Selected applications of dye-functionalized polymers prepared by ROMP

In the second major part of this concept paper, we show some examples from recent literature which illustrate the ability of ROMP as a pathway to functional materials and thereby focus on different applications where ROMP polymers have made a significant contribution. For sensing applications and bioimaging applications, dye-ROMP polymer conjugates are extremely well suited since they allow changing the solubility of dye molecules so that hydrophobic materials can be used in water. In addition, covalent immobilization of dyes reduces dye leaching, thereby improving, for example, sensor stability. In molecular probes, dyes can be combined with recognizable units and biocompatible materials and can therefore be used even in vivo. Another intriguing feature of ROMP polymers is that crystalline materials can be rendered amorphous which is of interest in electroactive applications because of improved film-forming properties. On the other hand, large aromatic units which are likely to self-assemble can be polymerized so that self-assembled structures are conserved. Finally, poly(norbornene) backbones are virtually non-absorbing to UV–Vis irradiation which makes them a suitable system for the polymerization of photoreactive and photochromic compounds.

Chemosensors

Copolymerization of dye molecules which change their optical properties upon an external stimulus (pressure/temperature change, presence/absence of an analyte) allows incorporating them into polymeric structures so that solubility and hydrophilicity can be adjusted to the application. Furthermore, self-assembly of amphiphilic block copolymers allows to incorporate dye molecules into micelles and hierarchical bulk structures. Typcally, norbornene polymers are characterized by a high polymerization yield, and easy monomer preparation, which makes combinatorial approaches possible.

As first example, azo dyes show a color change upon acidification which can be quantified as a bathochromic shift in the UV–Vis absorption spectrum. As opposed to radical polymerization techniques, ROMP is a facile way to incorporate these units into polymers and therefore, a number of polynorbornenes with azo dyes (**5**) have been synthesized [48–52]. In Fig. 3 monomers bearing such azo dyes as well as their color change at different pH-values in solution are shown.

Polynorbornenes with pendant 2-phenyl-1*H*-phenanthro[9,10-d]imidazoles showed a profound change of the photoluminescence of films upon exposure to HCl vapor [30, 31]. Furthermore, xanthene functionalized [via copolymerization of fluorescein, dichlorofluorescein, and eosin-bearing monomers (**6**)] ROMP polymers showed acid/base sensitive behavior when neat films were exposed to HCl or trimethylamine vapors, which makes them promising materials for sensing applications [40]. The copolymerization of norbornenes with pendant europium(III)-containing side chains like **7** led to red phosphorescent materials, whose luminescence lifetime can be used to detect small amounts of water vapor [66]. The structures of the used dye-functionalized monomers are given in Fig. 4.

The quenching of fluorescence by PET (photoinduced electron transfer) from moieties bearing free electron pairs, such as amines, can be used for pH measurements while tetramethylpiperidine-1-oxyl units act as quenchers which can be applied for the detection of radical species by recombination. This approach of combining dyes and responsive units on a polymer backbone has the advantage that different sensing mechanisms can be straightforwardly accessed by combining according monomers via ROMP. Furthermore, oligo(ethylenglycol)-functionalized norbornenes could be incorporated to render the resulting copolymers water-soluble. A key requirement is that the two functionalities are brought in proximity to each other, which was demonstrated by comparison of a blend system, random copolymers and block copolymers containing a perylene-based chromophore and trialkylamine and nitroxyl quenchers [21].

While several polymers derived from 8-hydroxyquinolinolato transition metal coordination compounds with pendant norbornenes have been obtained and characterized [58, 59, 62], it was only recently that polymers with pendant 8-hydroxyquinolines were used for the detection of Hg^{2+} and Cu^{2+} ions [26].

Bioimaging

In the last few decades molecular imaging has become one of the most important topics in the fields of chemical biology, nanomedicine, and noninvasive diagnosis of diseases. Due to the different solubility requirements in biological media, amphiphilic copolymers consisting of hydrophobic and hydrophilic segments in combination with recognition sites and optical labeling have gained

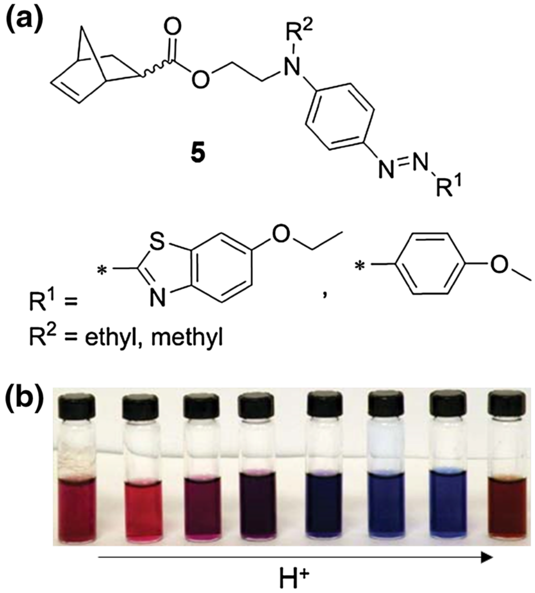


Fig. 3 **a** Norbornene monomers bearing aryl- and heteroarylazo dyes (**5**) and **b** their color change with increasing [H^+] concentration in DMF solution. Adapted with permission from [48]. Copyright (2009) Wiley–VCH

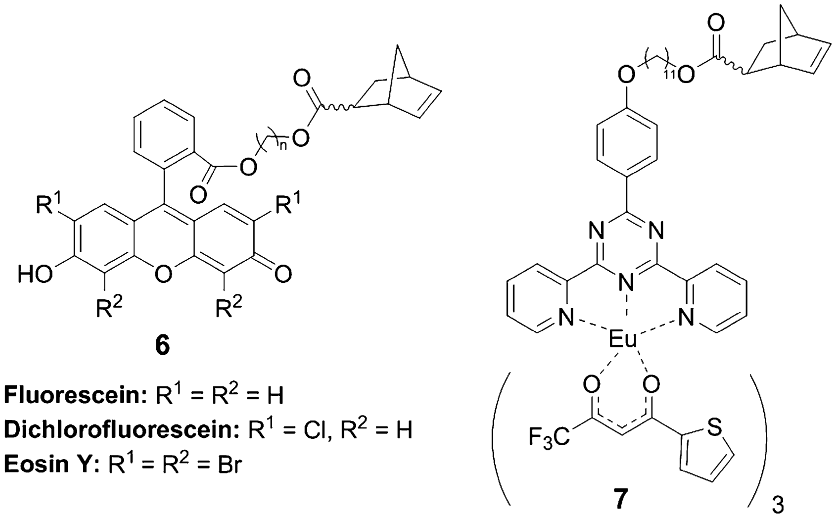


Fig. 4 Xanthene [40] and europium based [66] dyes used in ROMP sensor polymers

increasing importance in bioimaging, such as the visualization of tumor cells.

For example, Ohe et al. focused on the synthesis of amphiphilic ROMP polymers from a precursor to which oligo(ethylene) glycol chains were attached in a post-polymerization functionalization step using azide-alkyne click chemistry. Another monomer with a pendant 2-nitrobenzenesulfonyl group was incorporated to provide an orthogonal conjugation handle which was used to attach folic acid, glucosamine or an arginylglycylaspartic acid (RGD) peptide together with the near-infrared fluorescent (NIRF) dye indocyanine green (ICG) [84, 85, 88, 89]. The residual double bonds in these polymers whose number has been maximized (by using norbornadiene residues as ROMP-able group) were then perhydroxylated with K_2OsO_4 to form stable nanoparticles with a low critical micelle concentration in water. Different polymer architectures (for example **8**) were employed depending on the application.

Accumulation of these glycol chain bearing bioconjugated ROMP-based copolymers at tumor sites within several hours is possible and enables the visualization of cancer cells in vivo (mouse model, see Fig. 5) using NIRF whereby the glucosamine- or RGD-derivatized probes had the advantage over the folate-derivatized ones of not being accumulated in organs, such as the liver, but being preferably taken up by tumor tissue [88]. Belfield et al. attached two-photon fluorescent dyes and targeting RGD moieties to diblock ROMP copolymers with oligoethylene glycol chains via succinimide ester chemistry in a post-polymerization functionalization step [82]. These polymers form spherical micelles (about 100 nm diameter) in water which are able to target human $\alpha_v\beta_3$ integrin in glioblastoma cancer cells so that they can be visualized by two-photon fluorescence microscopy.

Chien et al. [44] prepared block copolymers to which peptide chains were attached in a post-functionalization step and furthermore, a FRET (Förster resonance energy transfer) donor and acceptor couple was introduced to the end of the polymer chains via termination with dye substituted alkenes [bearing fluorescein (**10**) or rhodamine (**11**)] (Fig. 6). Upon enzymatic hydrolysis by matrix metalloproteinases, which are overexpressed in certain tumor types, the peptide chains are cleaved so that the polymer chains form aggregates and resonance energy transfer takes

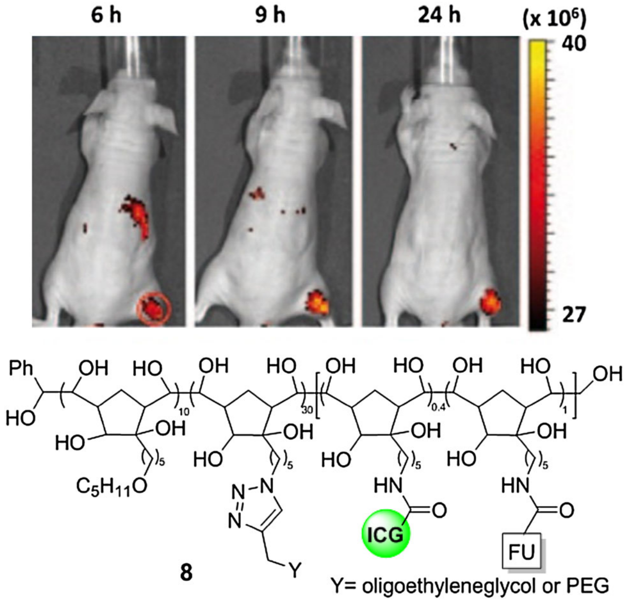


Fig. 5 Perhydroxylated polynorbornenes labeled with dyes and recognizable units used as near-infrared fluorescent probes for cancer cell labeling in a mouse model. *ICG* indocyanine green, *FU* functional unit. Adapted with permission from [88]. Copyright (2011) Wiley–VCH

place. Thus, enzymatic activity in tumor cells could be detected [92].

Organic electronics

While there are some approaches using olefin metathesis polymerization for the preparation of organic semiconductor polymers, even short PPV [poly(*p*-phenylenevinylene)] chains, which can be prepared by ROMP, were found to be insoluble without the help of solubilizing alkyl chains [6]. Therefore, several attempts to incorporate smaller electroactive units such as oligomers, emitters and hole- or electron-transporting side chains in ROMP polymers have been made. Some examples are shown in Fig. 7.

ROMP of **12** (Fig. 7) using a [Mo] initiator led to a polymer with a maximum electroluminescence efficiency of about 0.55 % [35]. In addition, copolymerization can improve the film-forming properties of electroactive compounds which was demonstrated for diphenylanthracene. While pure diphenylanthracene cannot be used in electroluminescent devices, the polymers prepared by Schrock et al. (**13**) were successfully applied in organic light-emitting diodes (OLEDs). Similarly, 3,6-bis-(9,9-dihexyl-9*H*-fluoren-3-yl)-9-alkyl-9H-carbazole (**14**) was used in ROMP polymers prepared with a [Ru] initiator leading to good film-forming properties, thermal stability and good device performance [36].

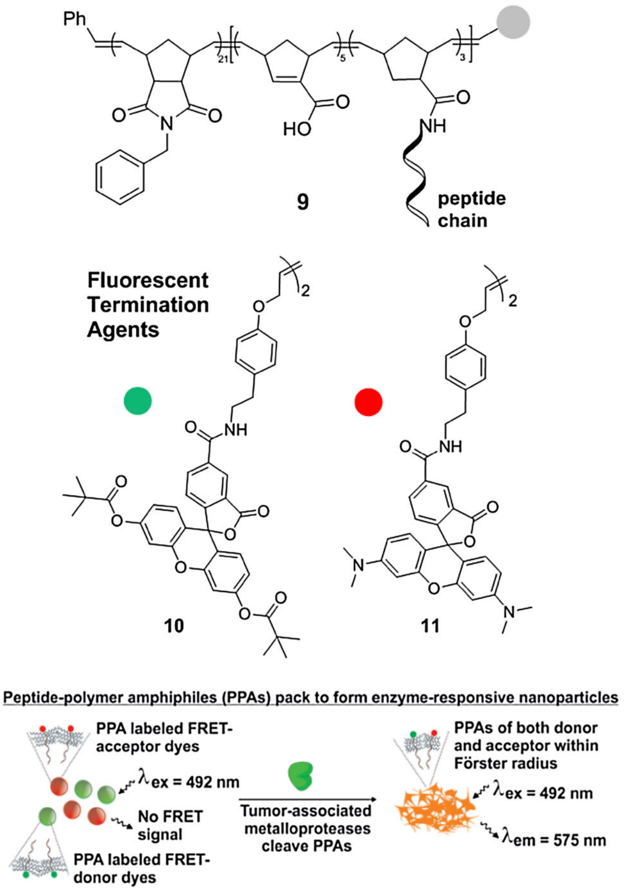


Fig. 6 Matrix metalloproteinase-responsive fluorescent nanoparticles. Adapted with permission from [92]. Copyright (2013) Wiley–VCH

An additional asset of ROMP in this context is that hole- (**15**) or electron transporting units (**16**) can be straightforwardly copolymerized (Fig. 7) which further improved device performance [15]. Post-modification of such polymers (sulfonation and epoxidation of the double bonds in the polynorbornene backbone) was attempted. The polyanionic sulfonylated polymer could be used for sequential layer-by layer adsorption with a polycation [poly(allylamine·HCl)], while ring-opening of the epoxides with various nucleophiles failed [17].

Polynorbornenes containing triphenylamines were used as emitter layers in OLEDs. The ester groups used to link these triphenylamine groups to the norbornenes, and consequently, the polymer backbone, are photolabile, rendering the resulting polymer photoreactive (via a photodecarboxylation reaction) which was demonstrated by photolithography of thin films so that different patterns could be inscribed to obtain structured fluorescent surfaces and patterned OLEDs [38]. In another study, LEDs with poly(norbornene)-triphenylamine as hole transporter and tris(8-hydroxyquinolinato)aluminum as emitter showed bright green emission with external quantum efficiencies (EQE) of up to 0.77 % (1.30 lm/W) for 20 nm thick films [39]. Cross-linking by UV irradiation decreased the EQE of these devices to 0.37 %. The substitution of ester groups by less polar ether anchoring groups for the triphenylamino functionality greatly enhanced EQE, lowered the operating voltage, and improved the stability of the device.

A polynorbornene random copolymer with phthalocyanine donor and C_{60} fullerene acceptor side chains (**17**) was synthesized for the application in solar cells (Fig. 8). Fluorescence quenching in this copolymer was enhanced compared to blend systems with a phthalocyanine-containing homopolymer. Although these copolymers can harvest photons with wavelengths up to the infrared region and the fluorescence spectra of the copolymers indicated a strong excitonic coupling, only moderate conversion efficiencies could be achieved so far [61]. Another approach for the preparation of PV cells was carried out by Marder et al. where perylene-3,4,9,10-tetracarboxylic diimides have been linked to a norbornene moiety. Two different perylene monomers have been synthesized; one where the monomer moiety is linked via one of the imide nitrogen atoms (**18**) and another one where the norbornene moiety is linked via the "bay"-area of the perylene (**19**, Fig. 8).

After polymerization, UV–Vis spectroscopy of the polymer containing imide-immobilized perylenes (**18**)

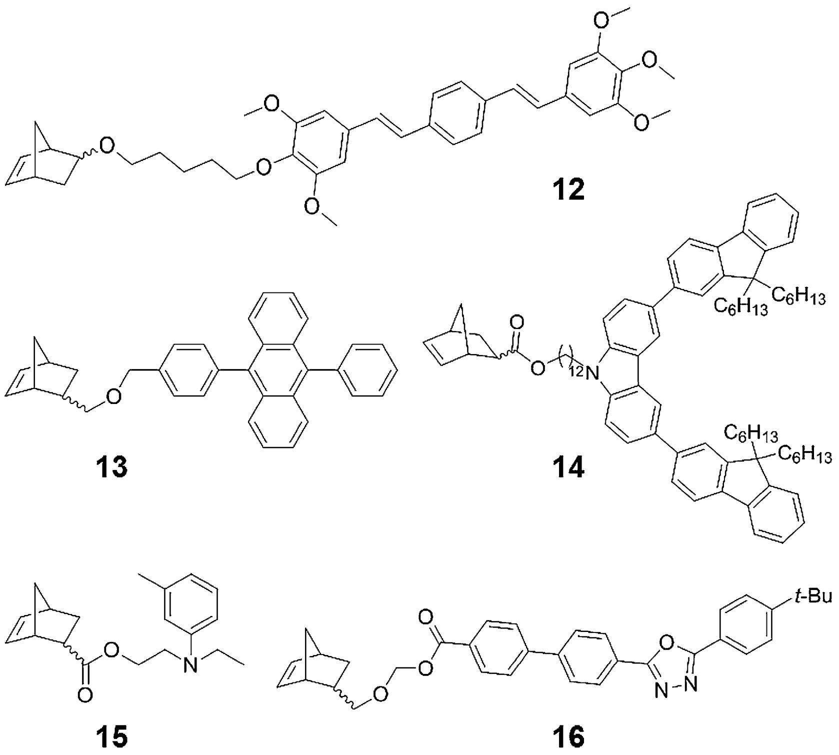


Fig. 7 ROMP monomers for OLEDs [15, 17, 35, 36]

suggests aggregation which was supported by according peaks in powder X-ray diffraction. This π-stacking led to n-channel field-effect transistor behavior, whereas the perylene linked to the polymer chains via the bay region (**19**) showed a monomer-like UV–Vis spectrum, no evidence for π-stacking and no measurable transistor behavior. Using polymers of **18** as acceptors in bulk heterojunction solar cells in combination with poly(3-hexylthiophene), low power conversion efficiencies were obtained. The best performing device made from poly-**18** ($R=C_{11}H_{23}$) had a PCE (photoconversion efficiency) of 0.38 %, whereas the PCE for polymers of **19** was one order of magnitude lower [23].

Generally speaking, the norbornene units necessary for polymerization result in a non-conductive polymer backbone which limits charge carrier transport, not only at a molecular level but also in the active layer which would be an explanation for the observed lower efficiencies in organic photovoltaics and lower performance in organic field effect transistors. However, ROMP is an ideal technique to combine different functionalities in one polymer backbone.

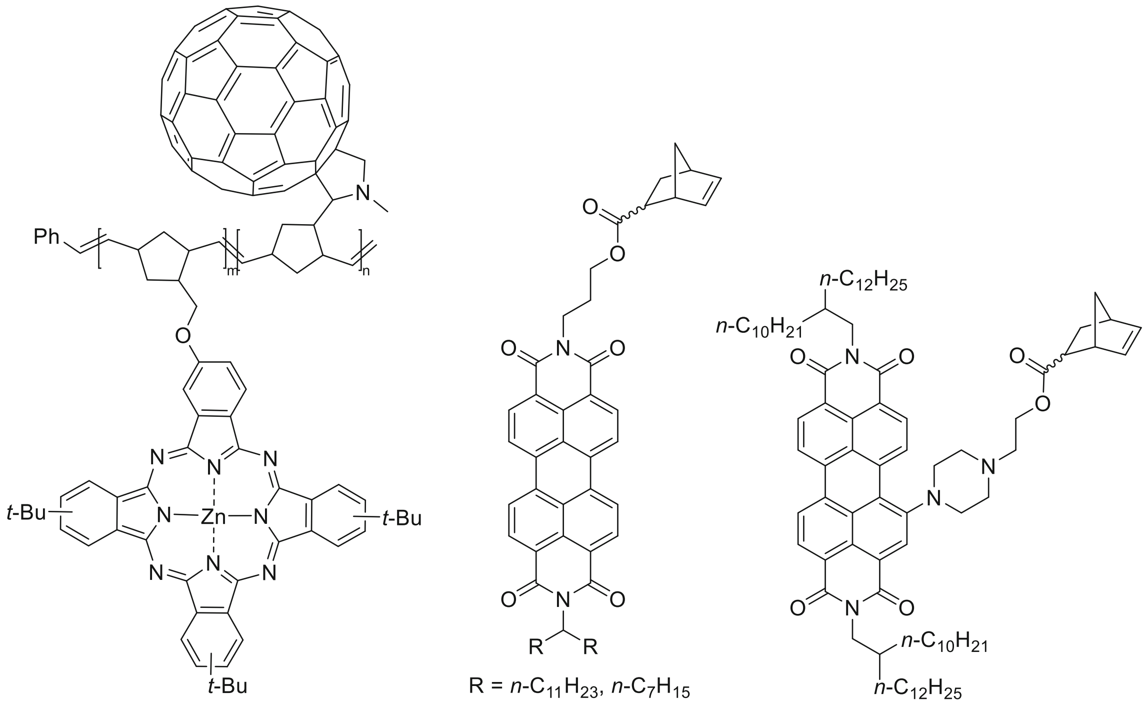
Poly(norbornene-*exo*-dicarboximide) bottle brush-type polymers decorated with a pendant azobenzene dye were employed as polymer hosts for a phenyl vinylene thiophene vinylene chromophore guest resulting in bi-chromophore electrooptic (EO) blend materials, which changed their refractive index in dependence of an electric field. By attaching different substituents to the azobenzene moieties (methoxy or cyano groups), the authors were able to improve π-electronic polarization and the EO coefficient which is a measure for the change in refractive index upon applying an electric field [49].

Flexible electrochromic devices were prepared from a ROMP polymer with pyrene and triphenylamine functionalities (**20**, Fig. 9). The double bonds of the polymer backbone were hydrogenated to improve the thermal and oxidative stability. Furthermore, the polymer is characterized by remarkable solvatochromism, excellent electrochemical stability and reversible electochromic behavior while adjusting the color (from yellow to green to dark blue) can be done by applying different voltages.

Self-assembly

By tuning the polymer structure via ROMP, it is not only possible to define the quantity and the site of the dye within the polymer chain, but also to build up regular structures, i.e. diblock- and multiblock-copolymers. Thus, it is possible to create dye functionalized micelles or hierarchically ordered bulk materials and thin films by the self-assembly of amphiphilic block copolymers in solution and in the solid state.

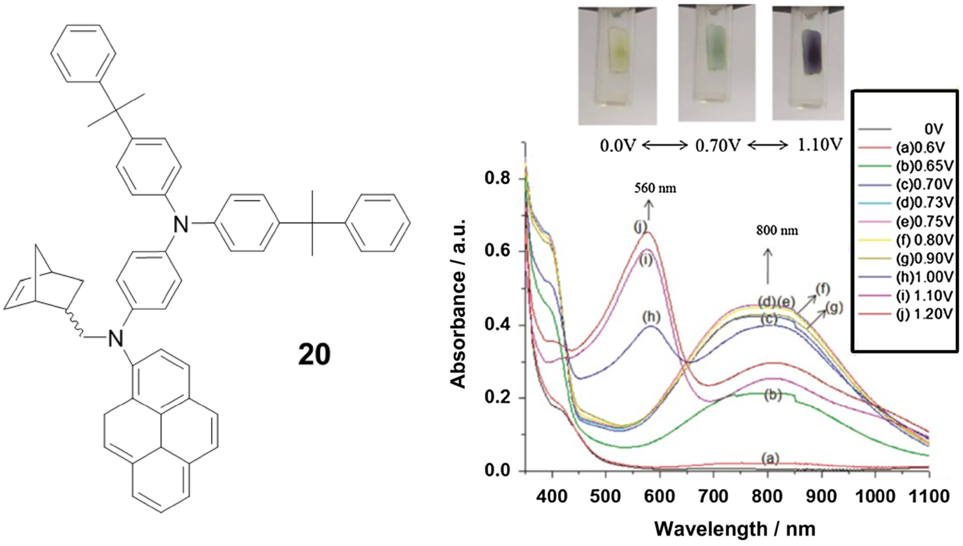
Xanthene dyes (fluorescein, eosin, and dichlorofluorescein) have been incorporated into the core of amphiphilic block copolymer micelles. The self-assembly process in methanol was found to be strongly influenced by the degree



17 **18** **19**

Fig. 8 Zn-porphyrine/fullerene random copolymer [61] and perylenebisimide monomers for the preparation of PV cells [23]

Fig. 9 Electrochromic ROMP monomer (**20**) and optical images and UV–Vis spectra of the resulting polymer. Adapted with permission from [29]. Copyright (2011) American Chemical Society



of ionization of the dye unit. The aggregation size was significantly smaller when the dye molecule was charged which is due to the ion pair formation of the charged molecule and the according counter ions, thus inducing strongly attractive dipole–dipole interactions. Even a minor amount of ionogenic functional units influenced the aggregation behavior drastically. The optical properties of the dye were preserved within the aggregates, which makes this material useful for sensor applications [47]. The eosin containing micelle system was also investigated via SAXS (small angle X-ray scattering) measurements in solution, whereby the pH-sensitivity of the eosin dye was preserved within the accrued micelles [45].

Using the different approaches outlined above, precise placement of the dyes in either the hydrophilic or the hydrophobic block as well as on either chain is possible while the ratio of hydrophilic and hydrophobic blocks can be adjusted simply by employing adequate monomer/initiator molar ratios so that tailor-made block copolymers can be achieved easily [21, 40–47]. In addition to the tailored design of highly specific materials for bioimaging and visualization of tumor cells, even unspecifically labelled, self-assembled nanoparticles can be applied for e.g. drug delivery as shown for rhodamine-decorated micellar nanoparticles which were accumulated preferably in cervical cancer cells [77] or tumor cells [43].

Another intriguing approach is to have polymerizable moieties which can be used to conserve a self-assembled structure which is, since self-assembly is a thermodynamically controlled process, a good strategy to obtain kinetically favored self-assembled intermediate structures which arise only for a short period of time by polymerization of a backbone.

One example is the polymerization of self-assembled conductive nanocoils with uniform diameter and helical pitch from a norbornene-appended hexa-peri-hexabenzocoronene (HBC) [25]. After polymerization, thermal rearrangement of these nanocoils into nanotubes at room temperature is no longer possible (Fig. 10). However, also the nanotubes can be obtained by post-annealing-ROMP of the self-assembled nanotubes. Furthermore, the π-stacked HBC arrays exhibited conductivity upon oxidative doping.

By adding norbornenes with an enantiopure side chain to the hexabenzocoronene-decorated monomers, instead of a racemic mixture of right and left- handed coils, either version could be obtained selectively [26].

Later, double-stranded polymeric ladder polymers using HBC as linker (**21**, Fig. 11) have been synthesized and self-assembled patterns were studied by scanning tunneling microscopy (STM) [27]. While the monomers arranged into a similar pattern with face-on morphology as observed for unsubstituted HBC, the ladder polymers attained a rod-like structure.

Perylenes are another class of polycyclic aromatic compounds which show interesting self-assembly behavior and were therefore also incorporated in ladder polymers (Fig. 11). Unlike for the hexabenzocoronenes, the perylene moieties were aligned in different directions and the resulting ladder polymers ended up to be amorphous as shown by TEM analysis [24]. The aggregation of perylenes is varying depending on the chemical environment and this in turn influences the optical properties of a material in different solvents and in film [22].

Generally speaking, the polymerization and furthermore stabilization of such self-assembled dyes with pendant norbornene residues does not influence the spectroscopical characteristics. Therefore ROMP of self-assembled compounds is a great way to increase stability and also to lock self-assembled structures.

Photoreactive materials

Materials which are photoreactive change their properties upon absorption of light. The incorporation of photoreactive dye molecules results in polymers which change their color (irreversible e.g. by photobleaching—or reversible in photochromic dyes), or alter their surface energy (and thus the wettability and chemical reactivity of the surface) or their solubility. This can be used for photoresists, to create relief structures or to influence the morphology of materials. Using photolithographic methods, most of these changes can be realized locally and thus functional patterns can be inscribed by light.

Two different reaction types can be applied: irreversible photoreactions induce a permanent change in the material's properties and reversible photoreactions create a platform of materials responsive on light as external stimulus.

Regarding irreversible photoreactions, several approaches have been exploited. Examples are the photoisomerization of benzylthiocyanates to benzylisothiocyanates [93], the photoisomerizaton of aryl esters [94–96] or amides [97] via the photo-Fries rearrangement, or the photocleavage of nitrobenzylesters (photo-acid generation) [98, 99], see Fig. 12.

The photochemistry of benzylthiocyanates (Fig. 12a) can be used to inscribe relief patterns into ROMP polymers by a subsequent addition of amines to the photogenerated isothicoyanate groups forming a thiourea bond [93]. However, exactly this chemistry can also be used to immobilize dye molecules in a blend of this polymer and polyfluorene. Following this approach, an amino-functionalized ruthenium complex—Ru(bipyridine)$_2$(5-aminophenantroline)(PF$_6$)$_2$—has been immobilized in thin films only in the irradiated areas leading to patterned fluorescent thin films as well as electroluminescent devices [100].

The photo-Fries rearrangement (Fig. 12b) causes a significant change in refractive index upon irradiation in the polymeric materials and thus can be used to create refractive index patterns with possible applications in optical data storage and transmission [94, 95, 101]. Refractive index changes up to $\Delta n = 0.01$ have been obtained in polynorbornenes bearing aryl amides as pendant groups [97]. In addition, the photogenerated aromatic hydroxyketones and aminoketones can be easily post-functionalized with dye molecules. Following this route, dansyl chloride, thiocyanatoiron, and hydrazones have been immobilized on the irradiated areas of polynorbornene dicarboxylic acid diphenyl ester [102] and fluorescamine using the corresponding phenyl amide functionalized polymer [97].

In the last years, also photoacid generators on the basis of the photocleavage of *o*-nitrobenzylesters (Fig. 12c) have

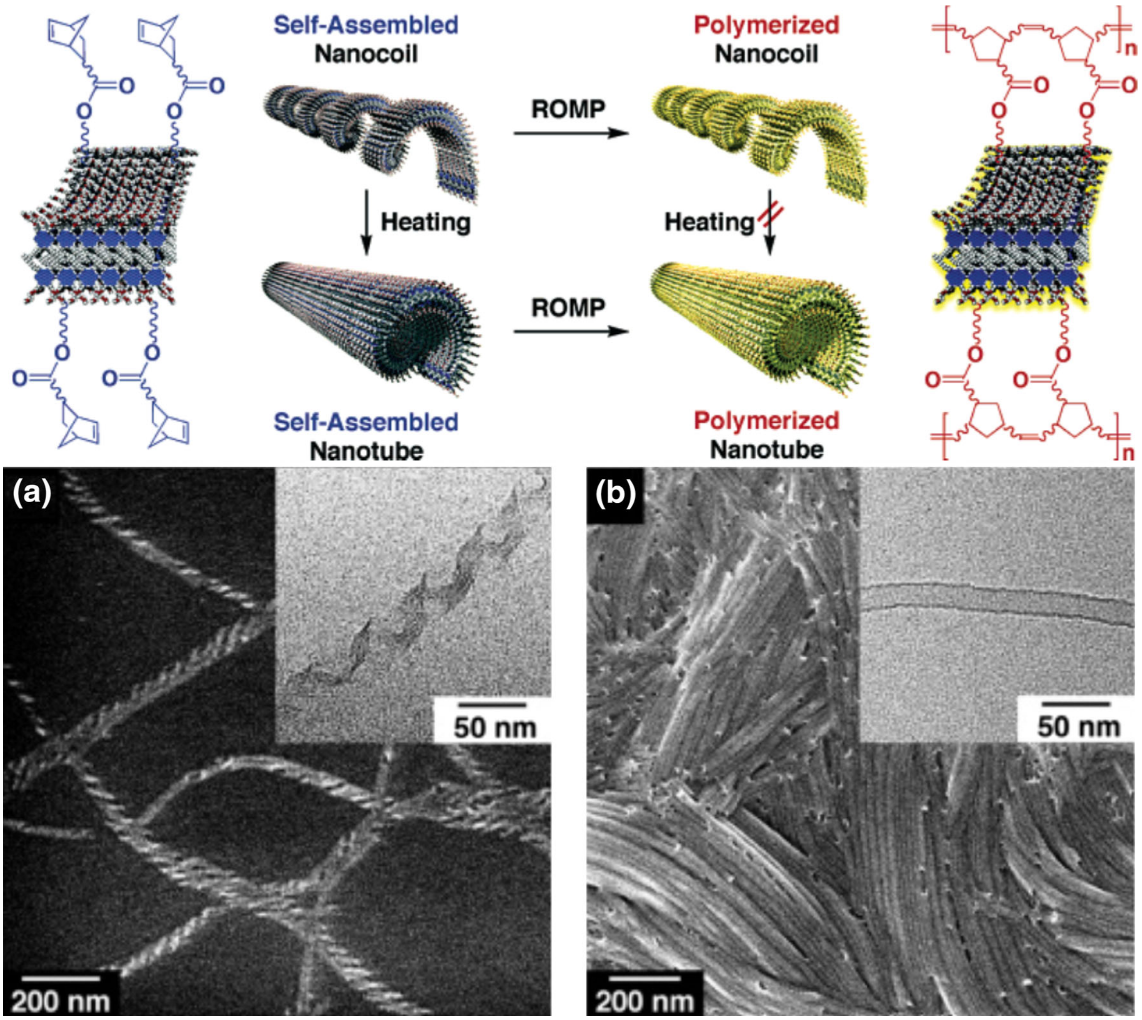


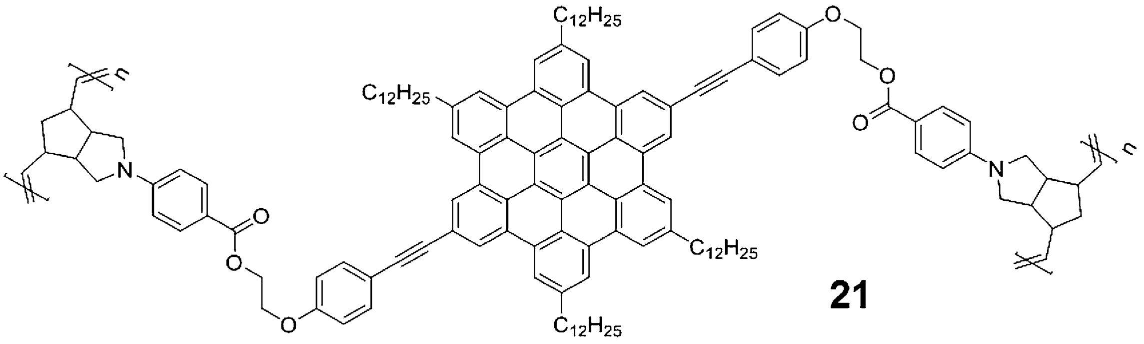
Fig. 10 HBC nanocoils (**a**) and nanotubes (**b**) which can be stabilized via ROMP. Adapted with permission from [25]. Copyright (2006) American Chemical Society

been explored in regard to refractive index patterns [99]. Hydrogels cross-linked with *o*-nitrobenzylester units can be de-crosslinked upon irradiation [103]. This was also used for dissolving thin films prepared by layer-by-layer adsorption technique by disturbing the electrostatic balance within these films [104]. The change in surface polarity due to the formation of the carboxylic acid can also be used to influence electrical characteristics of organic thin film transistors based on pentacene, either via influencing the growth of pentacene from the vapor phase [105] or influencing the charge concentration in the conductive channel [106].

Another example of a photoreactive polynorbornene system was a *tert*-butyloxycarbonyl-protected quinizarin-functionalized polynorbornene which could be deprotected with the help of a photoacid generator (TPSOTf, triphenylsulfonium triflate) leading to a bathochromic shift of the absorption maximum from 350 to 490 nm in combination with arising red fluorescence (570–610 nm) after cleavage of the *tert*-butyloxycarbonyl protecting groups [32]. However, in this case the photoinitiator was not covalently linked to the polymer main chain.

Photoreactions have also been used to cross-link micelles leading to stable nanoparticles using the photodimerization of cinnamoyl groups via a photoinduced [2+2] cycloaddition. These groups have been introduced by the copolymerization of dye-functionalized monomers into the hydrophobic core of amphiphilic block copolymer micelles [46, 107]. ROMP was also used to prepare a macrophotoinitiator (eosin)–coinitiator (dimethylaminobenzoate) system for the UV curing of acrylates with improved migration stability and biocompatibility which was confirmed by leaching studies and improved adhesion of osteoblast cells [41].

Photochromic compounds undergo a reversible chemical reaction which changes their absorption properties upon



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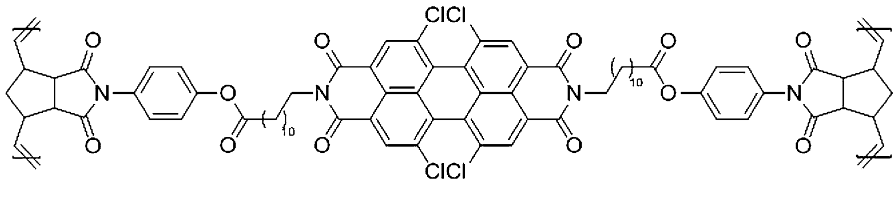

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Fig. 11 Ladder polymers based on HBC (**21**) [27] and perylenes (**22**) [24]

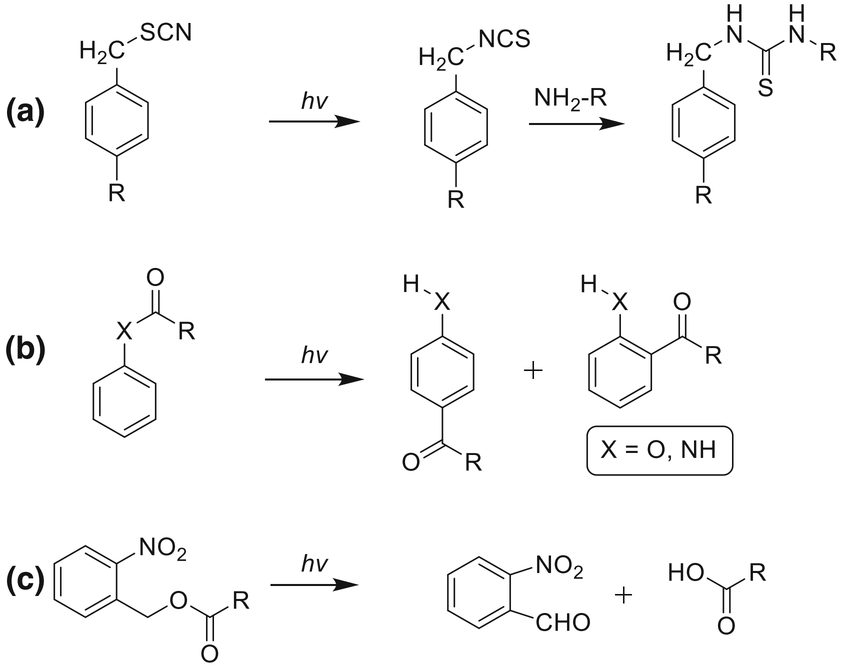


Fig. 12 **a** Photoisomerization of benzylthiocyanates to benzylisothiocyanates [93], **b** photoisomerizaton of aryl esters/amides [94–97] and **c** photocleavage of nitrobenzylesters [98, 99]

an optical stimulus. Potential applications for such compounds are optical data storage, ophthalmic lenses or photonic switches. Besides the two states being differently colored usually the two forms also significantly differ in other properties such as polarity or hydrophilicity.

The group of Branda used photochromic phenoxynaphthacenequinone to regulate the luminescence of porphyrines both introduced into ROMP polymers (**24**) via the monomer route, see Fig. 13 [108]. Isomer **23a** can quench the fluorescence of porphyrine as it is a much better electron acceptor. By switching between the two states **23a** and **23b** the luminescence can be reversibly turned on and off.

A series of homo- and copolymers containing various photochromic dithienylethenes (**25**) have been prepared by the same group. By blending or copolymerizing differently substituted dithienylethenes the attained color can be adjusted over a broad range (Fig. 14) and multiaddressable materials have been prepared with possible applications in multistate photochromic recordings and displays [109, 110].

The introduction of spiropyrans into ROMP polymers also results in photochromic materials [53, 111]. Irradiation with UV light (e.g. 365 nm, Fig. 15) initiates cleavage of the C–O bond at the spiro center followed by the *cis–trans* isomerization of the adjacent C=C bond leading to deeply blue colored merocyanines. This process is reversible for several reaction cycles and the back-reaction can be triggered thermally or by irradiation with long-wavelength light (>500 nm).

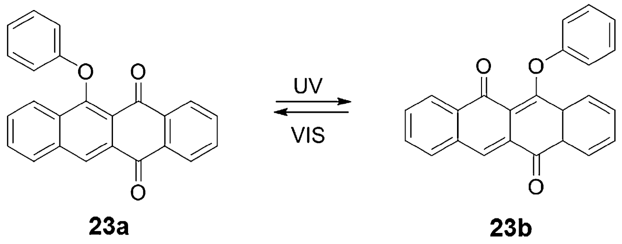
Amphiphilic random copolymers consisting of hydrophobic, hydrophilic, and spiropyran monomers were prepared and showed self-assembly to micellar structures. Upon UV irridation, the pendant spiropyran groups isomerize into their dipolar merocyanine form, which causes rupture of the micelles. Again, this process can be reverted by irradiation with longer wavelength light and this was used to encapsulate Nile Red serving as a lipophilic model substance for drug delivery applications, see Fig. 15 [57].

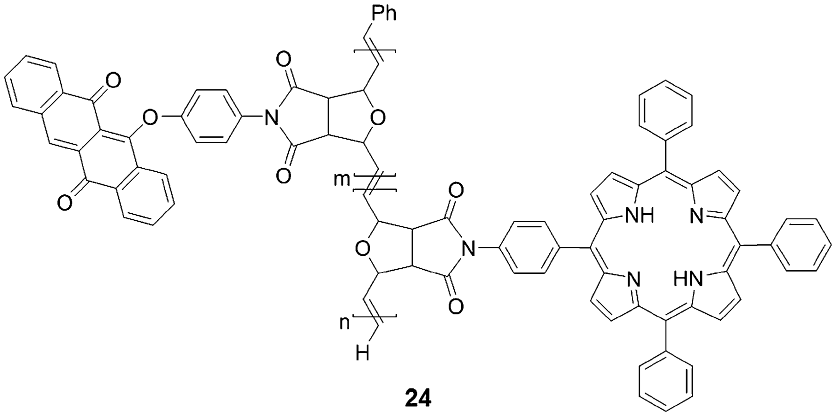
Structures with a resolution of down to 5 µm could be inscribed into thin films of a homopolymer containing pendant spiropyran units via contact photolithographic patterning [53]. Due to the dipolar nature of the formed merocyanines, a change in surface energy, confirmed by contact angle measurements [53, 54] and friction force microscopy [112] is imposed upon photoisomerization. The dipolar nature of the merocyanine zwitterions leads to them being favored in a polar environment whereas spiropyrans are the preferred form in an apolar environment. This was used as a probe for solvent polarity using capillaries equipped with polymer brushes prepared in a surface-initiated ROMP approach [55]. Recently, spiropyran-functionalized copolymers were used to control the charging properties from contact electrification in polymeric thin films [113].

Tomasulo et al. synthesized a spirooxazine-bearing polymer via ROMP. The absorption maximum for the closed oxazin ring is about 310 nm, whereas the open form has an absorption maximum of 440 nm. By transient absorption spectroscopy, it was demonstrated that UV irradiation opens the ring in less than 6 ns with a quantum yield of 0.09 in solution. However, the reisomerization speed was reduced from 20 ns up to 11 µs on the polymeric backbone [56].

Lambeth and Moore used a homopolymer containing an azo dye in its side chain for photoisomerization experiments to inscribe surface relief gratings with a laser wavelength of 488 nm using interference of linearly polarized light which resulted in a sinusoidal diffraction grating [50]. Furthermore, isotropic colloidal particles (prepared by gradual hydrophobic aggregation) were produced. These particles became deformed into ellipsoids when they were irradiated with linearly polarized light with the degree of stretching being proportional to the irradiation time. Different shapes could be inscribed in films of poly-**26** (Fig. 16) by proximity field nanopatterning, again at a wavelength of 488 nm [51]. *Cis–trans* isomerization of

Fig. 13 Photochromic ROMP polymers [108]





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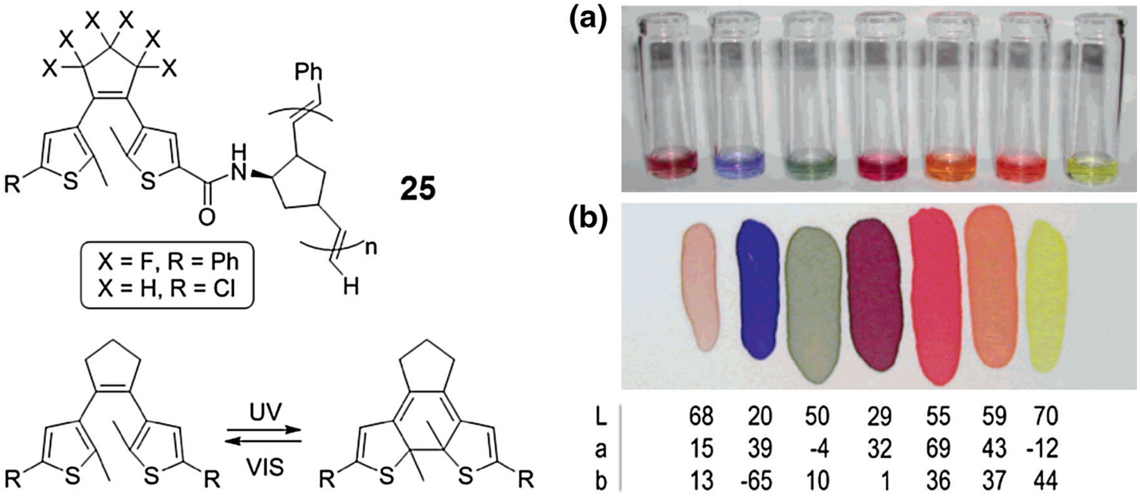

Fig. 14 Photochromic dithienylethene-based ROMP polymers. Adapted with permission from [109]. Copyright (2005) American Chemical Society

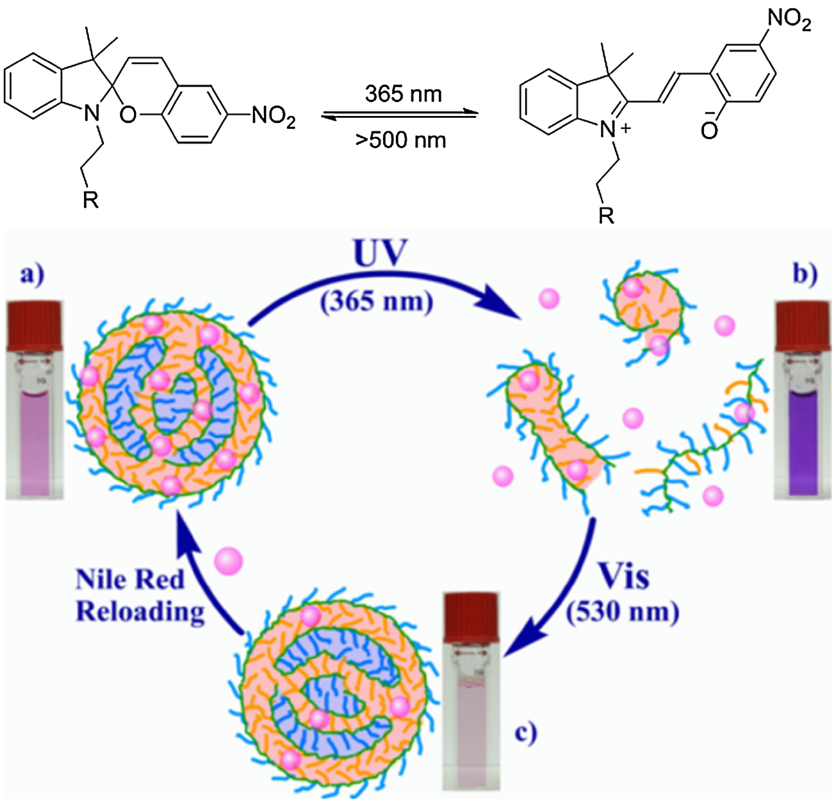

Fig. 15 Reversible photochromism of spiropyrans [53–55, 57] used for the light triggered encapsulation of Nile Red with spiropyran-functionalized random ROMP copolymers. Reprinted (adapted) with permission from [57]. Copyright (2012) American Chemical Society

such azo-dye bearing polymers was also achieved thermally [48].

Another reversible photoreaction is the photoinduced [$4\pi+4\pi$] cycloaddition of anthracene, which was explored for cross-linking and thermal de-crosslinking of polymeric materials. This photochromism was used for cross-linking of the macromolecules to generate a photolithographic pattern of thin polymer films. To achieve better solubility, copolymers with oligo(ethylenglycol) groups have been prepared and the principles to use this material as a photoresist have been shown [15].

Overall, a vast variety of photoreactive materials has been prepared via ROMP, owing not only to the high functional group tolerance of this polymerization technique

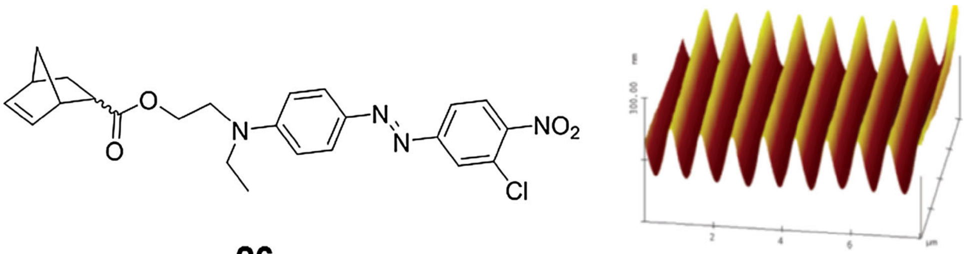

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Fig. 16 Azobenzene-derivatized monomer (**26**) and patterned photoisomerization of ROMP polymer thin film as visualized in an AFM image. Adapted with permission from [50]. Copyright (2007) American Chemical Society

but also to the beneficial properties for these applications such as good film formation and no interference with UV–Vis absorption of the functional dyes due to the poly(norbornene) backbones.

Conclusion

ROMP is a highly appropriate technique for the preparation of dye-functionalized polymers. The high functional group tolerance does not only allow the synthesis of polymers with a great density of functional groups on homopolymers, enabling the study of bulk properties such as photochromism, electron transport in devices or self-assembly leading to nanocoils, and ladder polymers. The living nature of ROMP, in addition to resulting in narrow polydispersity indices, also provides the opportunity to synthesize block copolymers while allowing precise placement of the dye molecules in each block. Furthermore, suitably derivatized initiators and termination reagents allow to selectively decorate either end of a polymer chain leading to precision polymers which have found use as polymeric sensor materials and furthermore, even as imaging probes which could be applied in vivo as well.

Moreover, reactive functionalities are easily incorporated in each of the three polymerization steps (initiation, propagation, and termination) and can be then converted in post-polymerization functionalization steps. Prominent examples include azide-alkyne click chemistry and active ester chemistry, which have the advantage that a large variety of suitably functionalized dyes are already commercially available. The inherent double bonds in ROMP polymers provide an additional opportunity for functionalization via thiol-ene or inverse electron demand Diels–Alder chemistry which both have been very recently also used for the immobilization of dyes on polymer chains.

We hope that this overview of recent developments of dye-derivatized ROMP polymers will stimulate further research in this exciting field.

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