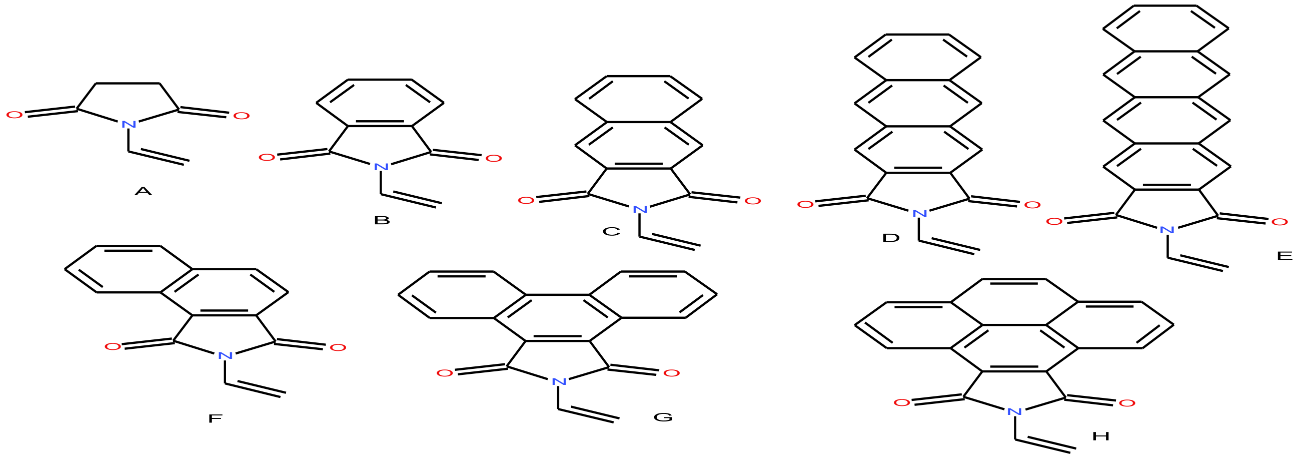
Vinyl Imide and Vinyl Aromatic Monomers and Polymers

By: Robert B. Login rloginconsulting.com

Thinking about new vinyl monomers that would contribute unique properties to copolymers such as color and florescence, I came up with the following:



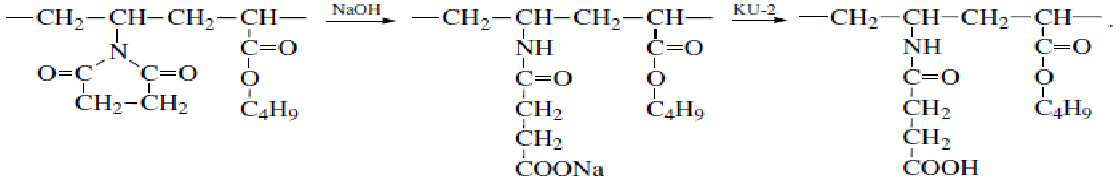
Scheme 1: Both A&B are well known vinyl monomers that have many references. C-H are just examples and not meant to be limiting, because many other polyaromatic structures could be possible.

Nikolayev, A. F., Tereshchenko, G. P., Salivon, N. Y., Pozdnyakova, F. O., & Proskuryakova, Z. G. (1972). Peculiarities of the copolymerization of N-vinyl succinimide with N-vinyl pyrrolidone. *Polymer Science USSR*, *14*(11), 2761-2764.

Murata, K., & Terada, A. (1966). Copolymerizations of 1-Phthalimido-1, 3-butadiene and 1-Succinimido-1, 3-butadiene. *Bulletin of the Chemical Society of Japan*, *39*(11), 2494-2499.

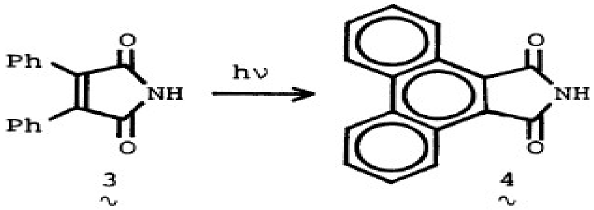
Abstract

—The testing results for copolymers of *n*-butyl acrylate with N-vinylsuccinimide used as medical adhesive materials are presented. These adhesives are designed to provide for the needed mechanical strength and also to be a conductor of physiologically active compounds. The copolymers under consideration are able to immobilize drugs containing amine groups. It is shown experimentally that vinylsuccinimide units in the copolymers with butyl acrylate can be easily and selectively transformed by alkali hydrolysis (without involving acrylate units) into units of N-vinylsuccinamic acid containing carboxyl groups, which makes it possible to immobilize physiologically active compounds on a polymer matrix such as this.



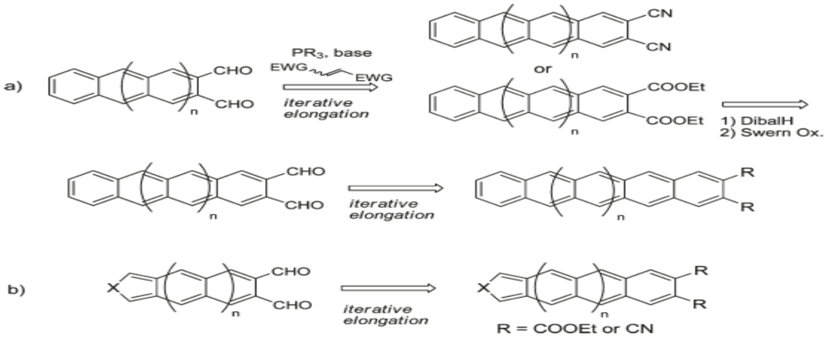
Sivtsov, E. V., & Lavrov, N. A. (2007). Synthesis of n-Butyl acrylate copolymers for medical adhesives. *Polymer Science Series C*, *49*(3), 245-250.

Synthesis references:

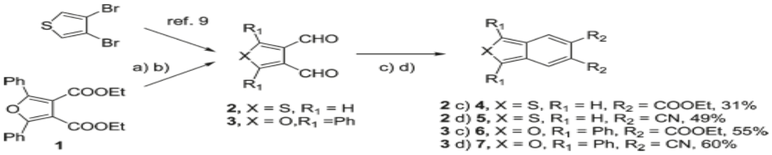


Izawa, Y., Yokoi, K., & Tomioka, H. (1981). Synthesis and Photochemical Reactivity of O-Alkylmaleimide. *Chemistry Letters*, *10*(10), 1473-1476.

SCHEME 1. **Iterative Elongation to Acene and Heteroacene**

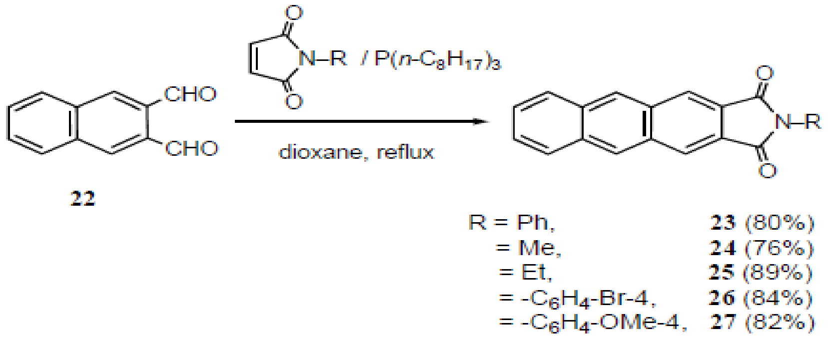


SCHEME 2. **Synthesis of Benzo[*c*]thiophene and Benzo[*c*]furan Diesters and Dinitriles**



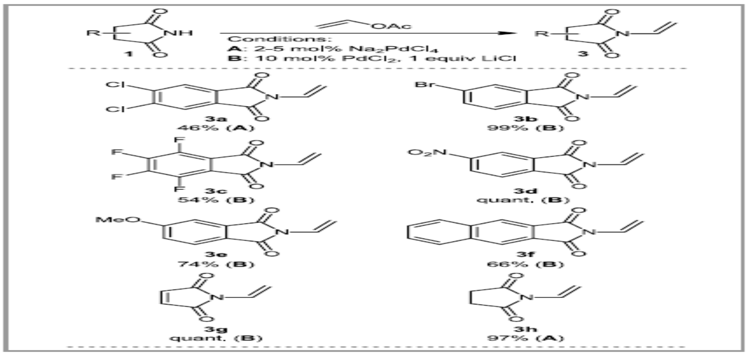
Reagents and conditions: (a) $LiBH_4$, $B(OMe)_3$, THF, 45 °C, 93%; (b) $(COCl)_2$, DMSO, then Et_3N, 94%; (c) diethyl maleate, $P(n\text{-}Oct)_3$ for **4** and **5**, PEt_3 for **4** and **5**, DBU, dichloromethane; (d) fumaryl nitrile, $P(n\text{-}Oct)_3$ for **4** and **5**, PEt_3 for **4** and **5**, DBU, dichloromethane.

Hsu, D. T., & Lin, C. H. (2009). Synthesis of Benzo [c] and Naphtho [c] heterocycle Diesters and Dinitriles via Homoelongation. *The Journal of organic chemistry*, *74*(23), 9180-9187.



Scheme 2. Synthesis of N-substituted 2,3-anthracenedicarboximides.

Oda, M., Shimosasa, H., Kumai, Y., Ohta, A., & Miyatake, R. (2014). An improved synthesis of arenedicarboximides by phosphine-assisted annulation of arene-1, 2-dicarbaldehyde with N-substituted maleimide. *Modern Chem*, *2*(4), 29-35.

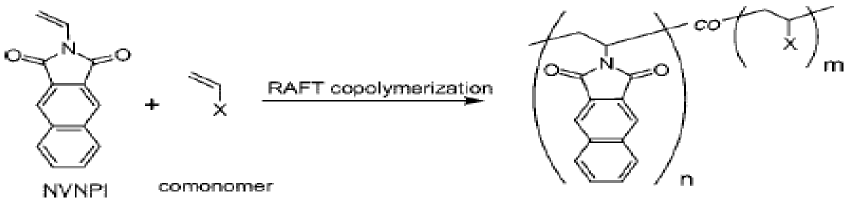


Scheme 3 Scope of the vinylation reaction. The reaction conditions used are given in parenthesis after the yield.

Haddadin, M. J., Agha, B. J., & Tabri, R. F. (1979). Syntheses of some furans and naphtho [2, 3-c] derivatives of furan, pyrrole and thiophene. *The Journal of Organic Chemistry*, *44*(4), 494-497.

Serrano, E., De Nanteuil, F., & Waser, J. (2014). Diester-substituted aminocyclopropanes: synthesis and use in [3+ 2]-annulation reactions. *Synlett*, *25*(16), 2285-2288.

Scheme 1. RAFT Copolymerization of *N*-Vinylnaphthalimide with Various Comonomers



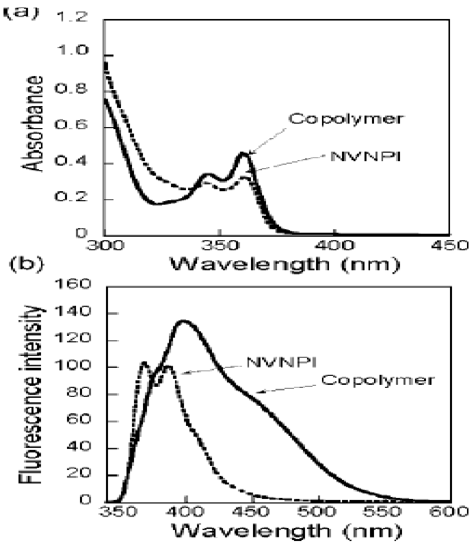


Figure 5. (a) Absorption spectra of NVNPI (dotted trace) and copolymer (solid trace, NVNPI/NIPAAm = 50/50, M_n = 10700, M_w/M_n = 1.22) in CH_2Cl_2 (concn = 4.6 × 10^{-5} NVNPI unit mol/L). (b) Fluorescence spectra of NVNPI (dotted trace) and copolymer (solid trace) in CH_2Cl_2 (concn = 9.2 × 10^{-7} NVNPI unit mol/L, λ_{ex} = 340 nm).

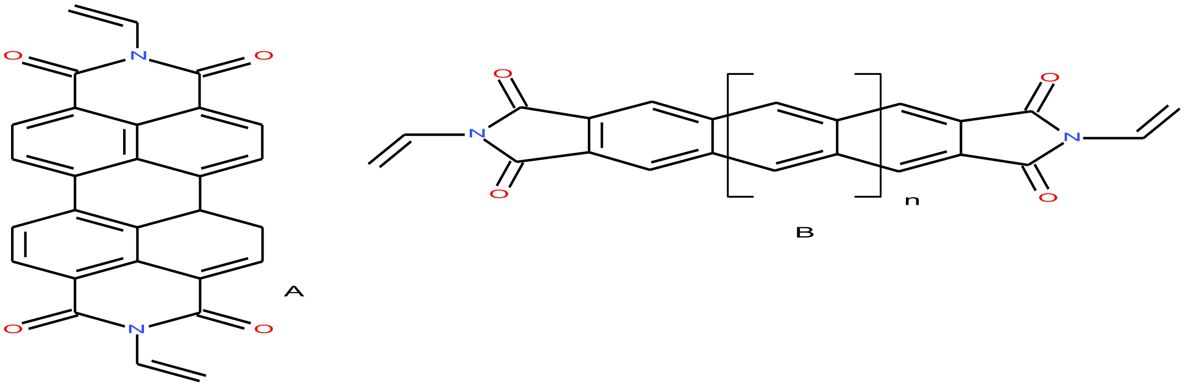
Maki, Y., Mori, H., & Endo, T. (2008). Synthesis of well-defined alternating copolymers by RAFT copolymerization of N-vinylnaphthalimide. *Macromolecules*, *41*(22), 8397-8404.

The above Maki et. al. reference shows that N-vinylnaphthalimide readily polymerizes by a free radical mechanism and readily copolymerizes with other vinyl monomers. With this in mind, can this and other monomers described in scheme 1 contribute other desirable properties to polymers? The ability of these monomers to contribute color and fluorescence to copolymers such as those with vinylpyrrolidone would result in water soluble or dispersable copolymers. Such copolymers might have desirable medicinal or cosmetic possibilities. Such as various colors and fluorescence. This could be a way of tagging copolymers so that they can be readily detected. There is a caveat to this idea, it is that the polyaromatics even with vinyl groups may not undergo free radical polymerization because the polyaromatic may interact itself with free radicals.

Stolka, M., Pearson, J. M., & Yanus, J. F. (1978). Process for preparation of 2-anthryl and substituted 2-anthryl functional monomers and polymers. US4117239

Yanus, J. F., Stolka, M., & Pearson, J. M. (1976). Polymerization of Vinylanthracene Monomers. 4. A Spectroscopic Study of the Anionic Polymerization of 1-, 2-, and 9-Vinylanthracenes. *Macromolecules*, *9*(5), 719-723.

Polyaromatic Crosslinkers:



Scheme 3: Two crosslinker examples of the many possibilities.

Würthner, F., Saha-Möller, C. R., Fimmel, B., Ogi, S., Leowanawat, P., & Schmidt, D. (2016). Perylene bisimide dye assemblies as archetype functional supramolecular materials. *Chemical reviews*, *116*(3), 962-1052.

Zhan, X., Facchetti, A., Barlow, S., Marks, T. J., Ratner, M. A., Wasielewski, M. R., & Marder, S. R. (2011). Rylene and related diimides for organic electronics. *Advanced Materials*, *23*(2), 268-284.

My idea is to use these divinyl crosslinkers to prepare gels for example hydrogels with n-vinylpyrrolidone. Said gels would be both colored and flouraphors. If microgels they could carry drugs and be visible for analysis.

Vinyl Aromatic Derivatives:

So far all the examples have been based on vinyl imides. So why not simply vinylate aromatics of interest? Some of these polymerizeable compounds are known.

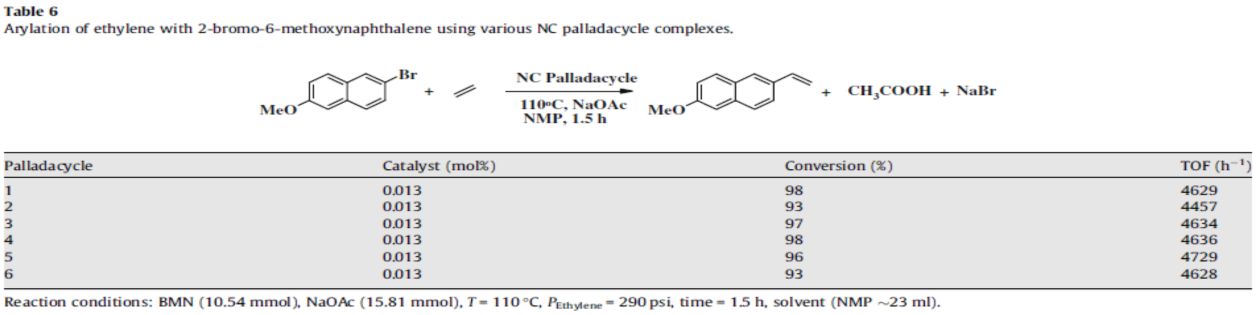
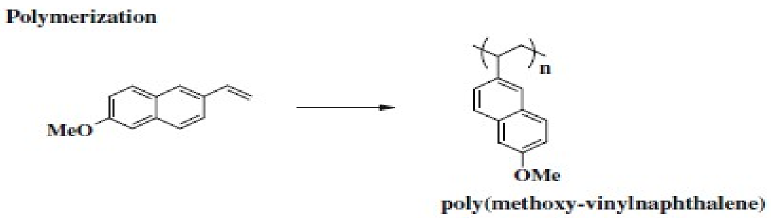


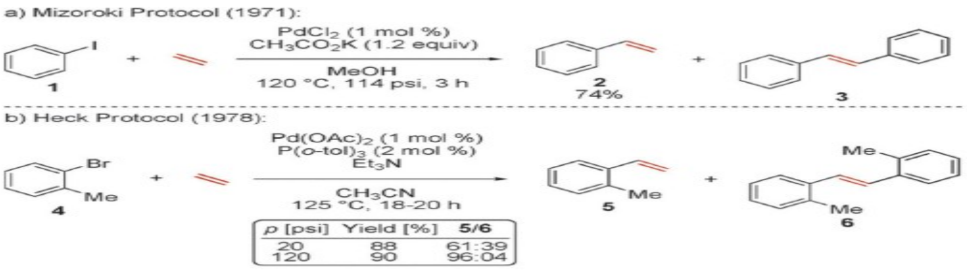
Table 6
Arylation of ethylene with 2-bromo-6-methoxynaphthalene using various NC palladacycle complexes.

Palladacycle	Catalyst (mol%)	Conversion (%)	TOF (h^{-1})
1	0.013	98	4629
2	0.013	93	4457
3	0.013	97	4634
4	0.013	98	4636
5	0.013	96	4729
6	0.013	93	4628

Reaction conditions: BMN (10.54 mmol), NaOAc (15.81 mmol), $T = 110\ °C$, $P_{Ethylene} = 290$ psi, time = 1.5 h, solvent (NMP ~23 ml).

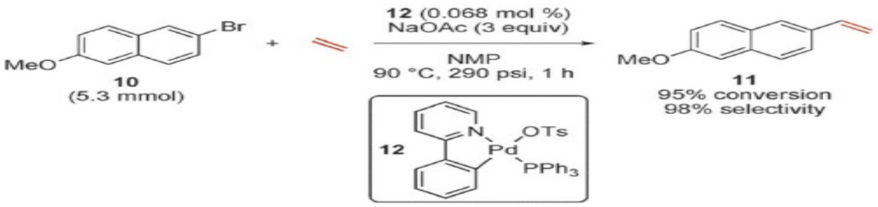


Atla, S. B., Kelkar, A. A., Puranik, V. G., Bensch, W., & Chaudhari, R. V. (2009). NC palladacycles in the Heck arylation of ethylene: Synthesis, structure and their reactivity. *Journal of Organometallic Chemistry*, *694*(5), 683-690.



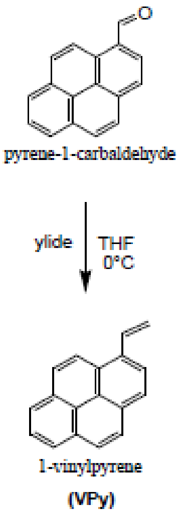
p [psi]	Yield [%]	5/6
20	88	61:39
120	90	96:04

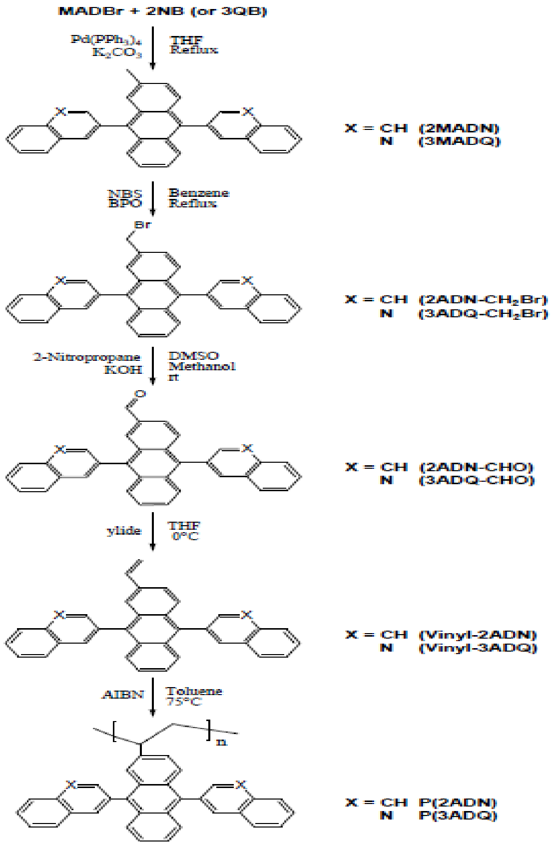
Scheme 1.
Palladium-catalyzed Mizoroki–Heck arylations of ethylene.



Scheme 3.
The C,N-palladacycle-catalyzed Mizoroki–Heck arylation of 2-bromo-6-methoxynaphthalene. NMP=1-methyl-2-pyrrolidone, Ts = 4-toluenesulfonyl.

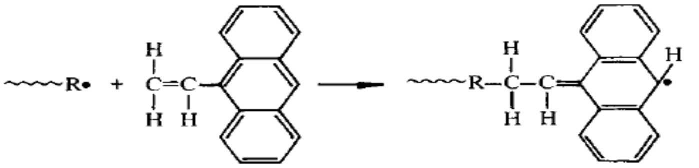
Saini, V., Stokes, B. J., & Sigman, M. S. (2013). Transition-Metal-Catalyzed Laboratory-Scale Carbon–Carbon Bond-Forming Reactions of Ethylene. *Angewandte Chemie International Edition*, *52*(43), 11206-11220.





Wang, J. (2013). Synthesis and characterization of conductive and soluble side-chain blue fluorescent polymers. repository.hkbu.edu.hk

respectively[2]. These results show that 9-vinylanthracene undergoes radical isomerization copolymerization with formation of polymer chains consisting mainly of 9-ethylidene-9,10-dihydroanthracene-derived units *), as shown in Eq. (1).



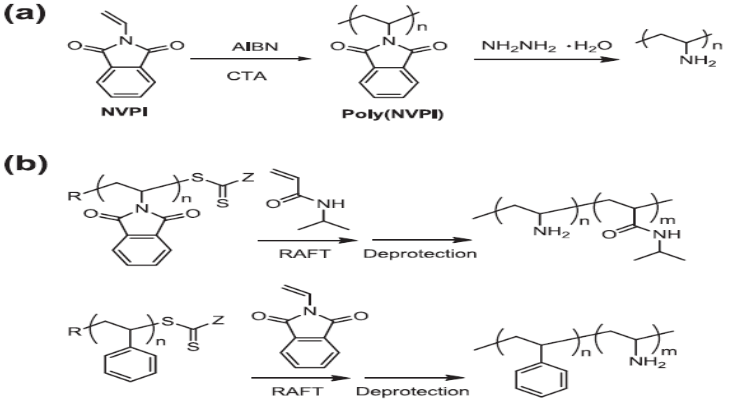
(1)

Takeuchi, K., Hanaoka, T. A., Arakawa, H., Matsuzaki, T., Sugi, Y., Takagi, S., & Doi, Y. (1989). Accelerated free? radical copolymerization of 9? vinylanthracene with methyl methacrylate using ethylaluminium sesquichloride. *Die Makromolekulare Chemie, Rapid Communications*, *10*(12), 645-648.

The same idea to use these aromatics to mark copolymers for ease of detection. A small quantity could do the job.

Vinylamines:

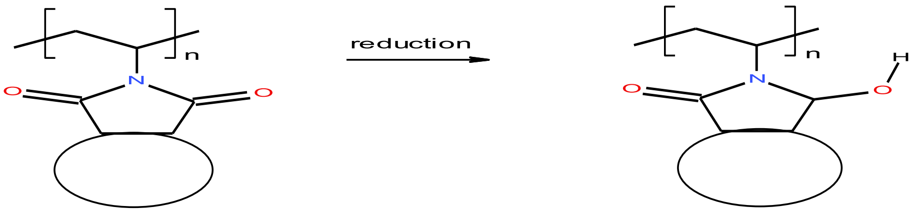
2828 K. Nakabayashi, H. Mori / European Polymer Journal 49 (2013) 2808–2838



Scheme 26. Synthesis of (a) well-defined poly(vinyl amine) and (b) amphiphilic and double-hydrophilic block copolymers having poly(vinyl amine) segments using RAFT polymerization of *N*-vinylphthalimide (NVPI), followed by deprotection.

The major method to add pendent primary amines to vinyl polymer backbones is to employ N-vinylforamide which is readily available. Such pendant primary amines can be protonated resulting in swollen cationic polymers or readily crosslinked to form gels that swell in acid but collapse in basic or neutral aqueous solutions. Such ability has been used as a way of delivering drugs. In addition, rigid copolymer with styrene might be useful as ion-exchange beads. Desirable weak acid compounds could be harvested from aqueous media then transferred to a stronger acid solution where they would be released and harvested. Said polyvinylamines in suitable solvents might be useful mild stripping agents capable of removing hair dyes. Polymeric primary amines can be employed to neutralize a wide variety of acidic medicinals for aqueous delivery.

Polyimide Reduction:



Scheme 2: Partial reduction of imides is in the literature.

MATSUKI, K., INOUE, H., ISHIDA, A., TAKEDA, M., NAKAGAWA, M., & HINO, T. (1994). Enantioselective reduction of meso-cyclic-1, 2-dicarboxylic anhydrides and 1, 2-dicarboximides: asymmetric synthesis of bicyclic lactones and hydroxylactams. *Chemical and pharmaceutical bulletin*, *42*(1), 9-18.

Miller, S. A., & Chamberlin, A. R. (1989). Highly selective formation of cis-substituted hydroxylactams via auxiliary-

controlled reduction of imides. *The Journal of Organic Chemistry*, *54*(11), 2502-2504.

Such pendent hydroxy lactams, would contribute greater hydrophilicity to said copolymers. This might be important to applications that require greater aqueous solubility.

I hope you found the above proposals interesting and worthwhile.

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