Chem 466 lecture #6 01/30/2014 @ Exam I, Thursday, Feb 6, 2014 - no office hours Feb 5 (Riof Woolg) - hourver Adriana will be available in 1423 on 1427 on 02/05 @ 3pm

aromatic Polyimides NO W-OLO-N-O-0-PO-Tradenames -· all aromatic inide + ether CKLO-DEHYDRATION DuPont) lineages - highly rigid + thermally state Sisofer uses as high T 2n+1 wie enamels · intractable once fully H20 insulating varnisher, Synthesized of prep'd in stages Fiberglass coating etc 0 ED. DH HO · a tractable poly (amic acid · once formed into desired STEP | ANNDATION physical form (coating, fiber etc. B>150°C to dehydrate v A in a polar high b.p. - 0 W-atz (NMP) or IN (DMAC) ayclize (aycloddrydration) with polyimide solvent, ps. ntl N+10) 1-0-O-NHS o +H2N-0 4,4'-diaminodiphengl ether pyromelliti dianhydride

5 Polymethanes + Polymeas · already seen : - a series of polyolefins polyethers, polycarbonates + polyesters having wethant + wea linkages to chain ends in Folmer B.J. B. et al. Adv. Mater 2000, 12, 874-878 (see Scheme 1) -a poly wethane of ethylene glycol tolnene diisocyanate Howatt + h cH3 catalyst + cH3 Howard + cH3 catalyst + cH3 Howard + cH3 Catalyst + cH3 Cotalyst + cH3 ntl 04 · Now, a polymethano-mea-ether copelymer example: urea XN40, 24 · Spandex, Ħ yora Dupont ~1959 wethane celasti fibers for wany rigid segment toxtiles, fabrics, pott, rubbery topes segment, also xtallne w/low (breakdown of wetbane linkages

I Cat. establishment of wrothave linkages prepolymens polyether n+1 H-0 (of H polyurea prepolymens cat: estetlishment (retrosynthetic step +2 breakdown of mea linkages) wethane linkings of rigid y poly signats y H, N-N, H + y+1 H -c, lot lot N=c=0 the polyether (poly(ethylene glycol) on poly (ethylene oxide)) is produced via ROP of ethylene oxide 1+10 KO 1+10 KO 1+10 KO 2) HO woll-up overall process, prep polyurea prepolymer, and prep polyether prepolymer, then copolymerize

Communications



loxane oligomers.^[3] Furthermore, hydrogen bonding between phenyl-urazole groups enabled chain extension of telechelic polyisobutylenes and crosslinking of polybutadienes.^[4] In these polymers, relatively weak association in combination with crystallization leads to physical crosslinks, which result in materials with improved properties.

Telechelic polymers functionalized with units that dimerize without forming crystalline domains will lead to concatenation of the building blocks and to selective formation of long linear chains. A high dimerization constant of the unit is a prerequisite for obtaining chains with a high degree of polymerization. Our group has described the strong dimerization of 2-ureido-4[1H]-pyrimidinones by quadruple hydrogen

bonding (Fig. 1) and the formation of linear polymeric chains of difunctional compounds.^[5] Recently, we have shown that this 2-ureido-4[1H]-pyrimidinone unit (UPy unit) is suitable for functionalization of low-molecular-weight telechelic siloxanes using a hydrosilylation reaction.^[6] However, this synthetic strategy is not generally applicable and requires protection/deprotection steps. Furthermore, functionalization of a trifunctional hydroxy-telechelic copolymer of ethylene oxide and propylene oxide with UPy end groups has been described that used a diisocyanate possessing controlled reactivity of the two isocyanate groups.^[7] But the use of this synthetic methodology is hampered by the possibility of covalent crosslinking.

Here we present the large-scale synthesis, from cheap commercially available reagents, of synthon 1 consisting of an UPy unit linked to a reactive isocyanate group. The electrophilic isocyanate can react with common nucleophilic end groups of telechelic polymers as hydroxy or amine groups (Fig. 1). To show the versatility of this approach OH telechelic poly(ethylene/butylene) was functionalized with 1 because it is almost completely amorphous and apolar, which increases the strength of the hydrogen bonds. Moreover, we will show that this concept is generally applicable to telechelic polyethers, polyesters, and polycarbonates, leading to a new set of supramolecular materials.

Building block 1 (2(6-isocyanatohexylaminocarbonylamino)-6-methyl-4[1H]pyrimidinone) was prepared from 2-amino-4-hydroxy-6-methylpyrimidine using a six-fold excess of 1,6-hexyldiisocyanate. When the conversion was complete, excess diisocyanate was recovered by distillation, and the product was isolated in a yield of 94 % at a scale of 200 g. Polymers 3 were prepared by refluxing dilute solutions (30 mM) of hydroxy telechelic polymers 2 in chloroform with a two-fold excess of building block 1, together with a small amount of dibutyltindilaurate as a catalyst. The conversion was determined with ¹H NMR spectroscopy, and after 10–16 h functionalization was complete (Scheme 1). Polymers 3 were obtained after a simple work-



Fig. 1. Schematic drawing of functionalization of telechelic polymers with quadruple hydrogen-bonded ureidopyrimidinone units.



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(C) Kinetics & reactivities of functional groups are independent of molecular size = D beyond monomer, dimer, trimer stage, rate constants are constant & overall rate of your depends upon - concentrations of reactive groups =D xxn slows as conversion increases (conc. decreases) 2 - reactivities of those groups the involved - whether catalyzed or not (- potential complications decreased solubility wincreased DPn · shift of equilibrium w/production or removal · increased viscosity of marcad DP. 26 mabr Br MA + raport ko "trapped "caged" Weguir. EA] + [B] concentrations + steady-state conc. of (MA BA kate of mahn = -d[A] = [ki] k [A][B] (2.2.9) formation dt [k] when kr << ki + ko text egn. (2.2.9 when kr << ki + ko -10 steady state conditions ki = ko k; [A][B] (2.2,10 = when ky >> ki+ko · discuss these relationships qualitativels, relative to user scheme

= kc [A][] (2.3.1) when catalyzed I the specific rate constants, orders of the 1xno + therefore the particular rate laws depend upon the particular 1xno (eg. toxt example (pection 2.3.3) uncatalyzed estentication 2^{mel} order in A 1st order in B) @ "" we will treat the kinetics gnalitatively De see Figure 2.4 from particular textbook example 2.2 time -> uncatalyzed dower commention of monomer (EAJ) A dower growth of DP than for catalyzed polymon However - catalysts do not alter positions of equilibria