

cross-linking is irreversible, it must be done while making the final part; and cross-linked rubber is difficult to reprocess. The 'cross-linking' step for styrene–diene block copolymers is instead a physical association of chains in the glassy polystyrene domains: the tendency of the two different chain sections to clump together, like with like. This association is robust enough to bear loads at room temperature, but is readily reversible upon heating.

Quite apart from their technological uses, block copolymers raise questions about the physics of macromolecular assembly and phase behaviour. How does the chain reconcile the wishes of the blocks to avoid one another when they are inextricably tied together?

Well-defined block copolymers assemble spontaneously into a variety of intriguing nanostructures, and other, aligned nanostructure arrays can be made using fluid flow or other fields⁵. Because of this, block copolymers have enjoyed great commercial success, as well as the ardent attentions of polymer physicists.

But block copolymers of amino acids have been little studied, largely because our synthetic methods do not have fine enough control to produce well-defined structures⁶. The same is true of the synthesis of block copolypeptides for use as biomaterials or as selective membranes — the potential advantages of the protein-like architectures have remained unrealized for want of adequate synthetic tools.

The method introduced by Deming¹ promises to change that. Deming treats the monomer of interest with the zero-valent nickel complex $\text{bipyNi}(\text{COD})$, where bipy is 2,2'-bipyridyl and COD is 1,5-cyclooctadi-

ene. Adding the NCA yields an initiator molecule that can be isolated and that remains active towards further ring-opening polymerization, and the target polypeptide can be prepared with essentially 100 per cent yield.

Claims of new 'living' polymerization methods must be evaluated with care. The ideal living polymerization is characterized by fast initiation and an absence of the termination and chain transfer steps that in most polymerization systems compete with propagation of the growing chain (Fig. 1). If these conditions are realized, all polymer chains begin growing at about the same time and continue to grow until the monomer has been exhausted. The average number of monomer residues per chain is then simply the molar ratio of monomer to initiator, and the distribution of chain lengths is described by Poisson statistics⁷.

Deming shows that these conditions have been met in the polymerization of NCAs by $\text{bipyNi}(\text{COD})$. The distribution of chain lengths is narrow, consistent with Poisson statistics, and the rate of polymerization is proportional to monomer concentration, indicating that the number of active chain ends remains constant throughout the reaction.

It is the absence of termination and transfer that makes living polymerization so powerful for synthesizing block copolymers. Because the growing chains remain active even after the monomer has been exhausted, adding a second monomer at that stage results in the growth of a second block distinct in composition from the first. Proper choice of monomers allows one to engineer the kinds of combinations of properties described above: rubbery and glassy; hydrophilic and hydrophobic; conducting and



100 YEARS AGO

In your account of the late Dr. Haughton ... I see no mention of a somewhat fantastic instance of his versatility – namely, his investigation into the most merciful way of hanging criminals. It was, I believe, entirely owing to him that the present method of the "long drop" was introduced. According to the older method the rope was so arranged that the culprit fell barely knee deep, all the rest of his body being in view above the scaffold. He died usually by strangulation, sometimes combined with apoplexy, after what seemed to be a protracted agony. Now, he is allowed to fall through some 10 feet, more or less, according to his estimated bulk and weight, and he dies with a broken neck more painlessly than virtuous persons in their own beds. The problem was to find out the length of drop that would suffice to break the neck bone, but would be insufficient to tear off the head. Dr. Haughton experimented on the tensile strengths of the spine and of the muscles, and he published a formula for the length of drop, dependent on the height and weight of the culprit. ... It should be mentioned that a case actually occurred in which the drop was too deep, and the head of the criminal became wholly detached, and the legal doubt arose whether under those circumstances the sentence of being "hanged by the neck" had been duly carried out. From *Nature* 25 November 1897.

50 YEARS AGO

In *The Condor* of July–August 1947 (49, No. 4), Dean Amadon gives an account of an investigation which he has made into the weight of the largest known bird. The ostrich (*Struthio camelus*), largest of living birds, was far surpassed in size by the elephant bird (*Aepyornis maximus*) of Madagascar; the larger of the New Zealand moas such as *Dinornis* were intermediate in size. The moas and elephant birds were exterminated by the natives of these islands and are known only from sub-fossil remains of skeletons, eggs and feathers. From *Nature* 29 November 1947.

Many more abstracts like these can be found in *A Bedside Nature: Genius and Eccentricity in Science, 1869–1953*, a 266-page book edited by Walter Gratzer. Contact David Plant. e-mail: subscriptions@nature.com

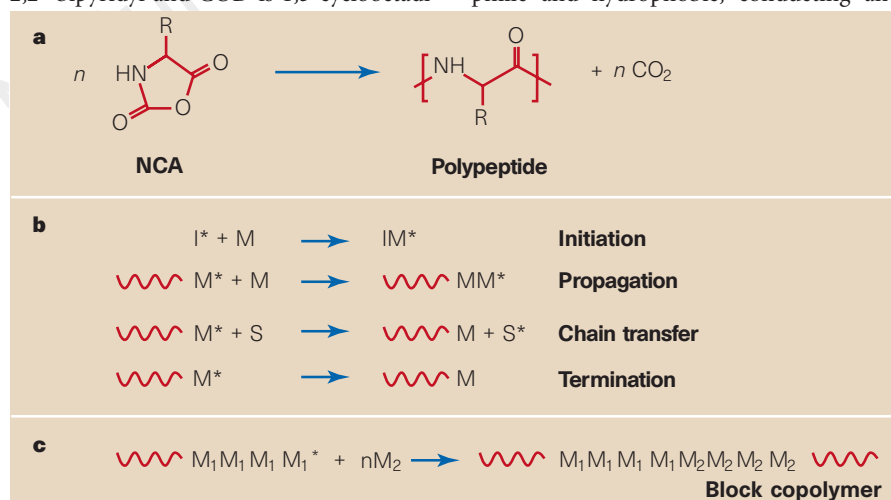


Figure 1 Synthesis of polypeptides by ring-opening polymerization of *N*-carboxy- α -amino-acid anhydrides (NCAs). a, Reaction of n moles of the NCA produces one or more moles of polypeptide and n moles of CO_2 . b, Chain-growth polymerizations involve initiation, propagation, chain-transfer and termination steps. Here the asterisk is an active species (derived from initiator (I) or monomer (M)) capable of further monomer addition, and S is a solvent or other species that ends the growth of one molecular chain and starts the growth of another. In living polymerizations, the termination and transfer steps are absent. c, Block copolymers are formed by the polymerization of the first monomer (M_1) to exhaustion, followed by the addition of a second monomer (M_2).