Hot melt adhesives have been known for centuries. Historically, mixtures of natural waxes, rosin, pitch, and other naturally occurring substances were used alone or in mixtures to produce sealing compounds for a variety of applications. It was not, however, until the early 1950s that hot melts based on synthetic polymers appeared in the marketplace.

Traditionally, as now, hot melts usually have been made by compounding existing high molecular weight polymers with low molecular weight resins to achieve the desired balance of properties. A great diversity of hot melts is now available from synthetic resins and polymers based on petroleum feed stock. Of all these, it is the compounded polyamides and polyesters which provide hot melts with the best properties.

The chemistry for these two classes of polymers goes back to the pioneering work of Wallace Carothers at DuPont which led to the development of nylon 6-6, poly(hexamethylene adipamide), the first man-made fiber. Carothers also investigated the aliphatic polyesters, but found them too low in melting point to serve as fibers. In England, however, J. R. Whinfield and J. T. Dickson of Calico Printers Association [British Patent 578,079 (1946)] developed polyesters from aromatic dibasic acids, including polyethylene terephthalate (PET), now the major synthetic polymer for fibers.

Most polyamides and polyesters are condensation polymers, produced by reacting dibasic acids with diamines to produce polyamides, or with diols to make polyesters. If derived from dibasic acids, the chemical structures can be represented as follows:

$$\left[\begin{array}{c}
O \\
\| \\
\| \\
\end{array}\right]_{n} \quad \text{Polyamide}$$

$$\left[\begin{array}{c}
O \\
\| \\
\| \\
\end{array}\right]_{n} \quad \text{Polyester}$$

If produced by ring opening of caprolactam or other lactam, the polyamide structure is:

$$\left[\begin{array}{c}
O \\
\| \\
\| \\
\end{array}\right]_{n}$$

In homologous series of polyesters and polyamides, the melt points, $T_m$, of polyesters are significantly lower than those of polyamides. As the proportion of carbon atoms in the main chain is increased, the melt points of polyam-
ides decrease while those of polyesters increase, both approaching the melt point of polyethylene as shown in Fig. 1.

The low melt points of polyesters are associated with the flexibility of the C—O chain bond and the low heat of fusion. The substantially higher melting point of the polyamides are the result of intermolecular hydrogen bonding across amide groups of adjacent molecules.

The melt point is also affected by the spacing of the polyester and amide groups since this determines the crystal structure of these polymers. The even-number carbon chains have higher crystallinity and therefore higher melt points. This trend is shown in Fig. 2 for polyesters made from decamethylene glycol and dibasic acids of varying chain lengths and for polyamides made from sebacic acid and diamines of varying chain length.

**POLYAMIDES**

Because the polyamides and the polyesters developed for fibers are too high-melting and too fast-setting to be used for adhesives, chemists have made copolymers to lower the melt point and increase the set time of these two classes of polymers. Today most of the polyamides and polyesters used in hot melt adhesives are based either on monomers not used for fibers or, more commonly, on copolymers. The most common monomers for hot melt polyamides are:

- **Dibasic Acids:**
  - Dimer acid (dimerized fatty acids).
  - Dodecanedioic acid.
  - Sebacic acid.
  - Azelaic acid.
  - Adipic acid.
- **Amino Acids and Lactams:**
  - Caprolactam.
  - 11-Aminoundecanoic acid.
  - Dodecalactam.
- **Diamines:**
  - Ethylene diamine.
  - Hexamethylene diamine.
  - Diethylene triamine.
  - Triethylene tetramine.
  - Piperazine.
  - Dipiperidyl propane (Dipip).
  - Polyoxypropylene diamine.

From these monomers have been developed a large variety of polyamides, which can be divided into four classes:

1. Polyamides made from lactams and amino acids.
2. Polyamides from condensation reactions of short chain dibasic acid and diamines.
3. Polyamides from long chain, vegetable oil-derived dibasic acids and short chain diamines.