# Dual Wall Heat-Shrinkable Tubing with Hot-Melt Inner Layer

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Heat shrinkable tubing with a meltable inner layer (dual-wall heat-shrinkable tubing) protects joints and connections in wiring harness connection with high adhesion, and has been widely used in electronics products and aircrafts. The application of the tubing has been extended to automotive wiring harnesses due to its easy handling and waterproof performance, and tubing that can be applied to complicated harness configuration is in high demand. To meet this demand, we have developed a new dual-wall heat-shrinkable tubing that shrinks at a low temperature and stays long. We optimized the shrink behavior and mechanical properties of the outer layer by controlling resin blending, and the flow and adhesion of the inner layer by applying the molecular design method and polymer alloy technology.

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Keywords: heat-shrinkable tubing, hot melt adhesive, electron beam irradiation, cross-linking, polymer alloy

## 1. Introduction

Heat-shrinkable tubing is a tube that shrinks in a radial direction when heated. It is widely used in the electronics, automotive, aerospace, and other industries for electrical insulation and mechanical protection of wire connections, corrosion protection of metal pipes, and many other purposes. Since 1964, Sumitomo Electric Industries, Ltd. has been manufacturing and supplying heat-shrinkable tubing under the trade name of SUMITUBE. In the 1980s, we developed dual-wall heat shrinkable tubing consisting of a hot-melt adhesive inner layer and heat-shrinkable outer layer, and started production and sales. When dual-wall tubing is heated, the adhesive inner wall melts and flows to conform to the object to be covered and thus protects the object providing a water tight environmental seal. Due to such excellent and reliable sealing performance, dual-wall tubing is widely used in electronic devices, aircraft, and many other types of equipment.

In the field of automotive in particular, customer demand for higher heat resistance (125°C) dual-wall tubing is increasing.

This paper describes the development of a new type of dual-wall tubing that can be used to protect automotive wiring harness connections.

## 2. Background and Target of the Development

Conventional dual-wall tubing is used to protect one-to-one wire connections in general. The tubing can be shrunk with hot air or other heating device (250-350°C) without any difficulty. On the other hand, for protecting automotive wiring harness connections, it is required to meet the following four specific conditions:

(1) Since the tubing is used to protect one-to-plural wire connections having a large size gap, the shrinkage characteristics of the tubing must be optimized so that it fits tightly to the irregular outer contour of the connections. Otherwise, the tubing will slip out of place and would not be able to protect the connections from water immersion (Fig. 1) at a service temperature of 125°C.

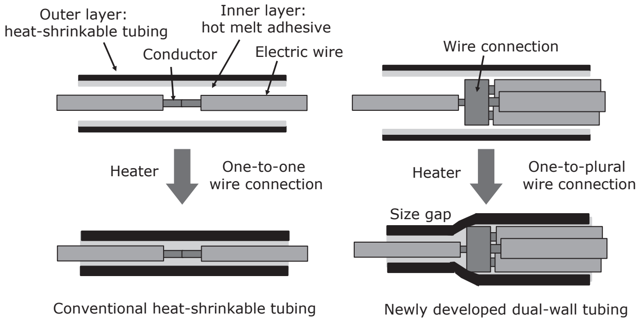

Fig. 1. Schematic illustration of wire connections covered with conventional and new dual-wall heat-shrinkable tubing

(2) Shrinking the tubing to a temperature higher than necessary will damage the insulation material of wire such as polyvinyl chloride (PVC)*1. It is therefore necessary to shrink the tubing at a relatively low temperature.

(3) An automated shrinking machine is used to process a large quantity of wiring harness splices with dual-wall heat-shrinkable tubing in order to enhance efficiency and eliminate any inconsistencies in the work. The process is required to minimize the heat-shrinking time and achieve high reproducibility.

(4) The tubing is required to have mechanical strength high enough to protect the wire connections from damage due to physical contact with other components during vehicle operation (Table 1).

To prevent PVC wires from thermal degradation during heat shrinking, the process temperature must be controlled to 100°C or less. To meet the above requirement, we measured the maximum heating temperature and time in the automatic shrinking machine and found that the tubing can be heated to 135°C for one minute. When the tubing is heated to this temperature, its outer layer must shrink completely, while the inner layer is required to flow and conform to the irregular outer contour of the covered object. At a service temperature of 125°C, on the other hand, the tubing is required to show proper insulation and sealing performance without moving both the tube and adhesive out of position. The development target for the material to be used for the new tubing and its target characteristics are shown in Tables 2 and 3, respectively.

Table 1. Difference in specifications between conventional and new tubing

| | Conventional tubing | New tubing |
|---|---|---|
| Use | Electronics, aircraft | Automotive wiring harness |
| Object to be covered | One-to-one wire connection | One-to-plural wire connection (size gap between both sides) |
| Inner layer | Easy-to-process resin | Resin with appropriate flowability and adhesiveness |
| Outer layer | | Hard resin having appropriate shrink characteristics |
| Shrinking method | Use of hot gun (manual work)<br>Small quantity | Shrinking machine (continuous shrinking)<br>Large quantity |
| Shrinking condition | Heating to high temperature for a long time to ensure sufficient shrinkage | Since the object to be covered consists of a PVC wire, the maximum allowable heating temperature is limited.<br>The shrinking time must be minimized to efficiently cover wire connections in bulk. |

Table 2. Development target for new tubing material

| | | Condition/item | Target |
|---|---|---|---|
| Inner layer | When shrinking | Shrinking by heating to 135°C for 1 minute | Percentage of heat shrinkage: 75% min.*[2] |
| | When using | No positional displacement after exposure to 125°C for 1000 h | Percentage of heat shrinkage: 20% max.*[2] |
| Outer layer | When shrinking | Fluidization when heated to 135°C for 1 minute | Conformance to the irregular outer contour of the objecton completion of shrinkage |
| | When using | No fluidization after exposure to 125°C for 1000 h | No fluidization |
| | When using | Adhesion to PVC, conductor, and outer layerHigh adhesion strength at normal temperature | Relative adhesion force 70% minimum of the metal-adhesion strength of conventional tubing. |

Table 3. List of target characteristics of new tubing

| Item | Condition | Target value |
|---|---|---|
| Mechanical characteristics | Tensile strength | 10.4 MPa min. |
| | Tensile elongation | 300% min. |
| | Coefficient of elasticity | 400 MPa |
| | Piercing strength (V-shape blade/thrusting in) | 450 N min. |
| | Thermal shock 225°C × 4 h | No crack generation |
| | Heat resistance 130°C × 7 d | No crack generation |
| Electrical characteristics | Dielectric strength | 15 kV/mm min. |
| | Volume resistivity | $1.0 \times 10^{12}$ Ω•cm min. |
| Chemical characteristics | Flammability | SAE J1128<br>Self extinction of flame within 70s |
| Sealing properties | Original | Leakage current 0.25 µA max. |
| | 125°C × 1000 h after heat-aging | |
| | Oil resistance Immersing in brake oil for 2 h | |
| | Oil resistanceImmersing in automatic transmission oil for 2 h | |

## 3. Development of Outer Layer Material Having Optimal Composition

### 3-1 Manufacturing process of heat-shrinkable tubing and principle of shrinkage

The manufacturing process of heat-shrinkable tubing is shown in Fig. 2. As shown in this figure, the manufacturing process consists of three steps: extrusion, electron beam*[3] irradiation, and expansion. In the extrusion process, resin is extruded into tubes shape. In the electron beam irradiation process, the tubes are crosslinked. In the expansion process, the crosslinked tubes are softened by heating and then internal pressure is applied to expand the tubes in a radial direction. Finally, the tubes are cooled and solidified as heat-shrinkable tubing.

The principle by which heat-shrinkable tubing shrinks when heated is shown in Fig. 3. When an electron beam is delivered to crystalline resin*[4] consisting of both a crystal-

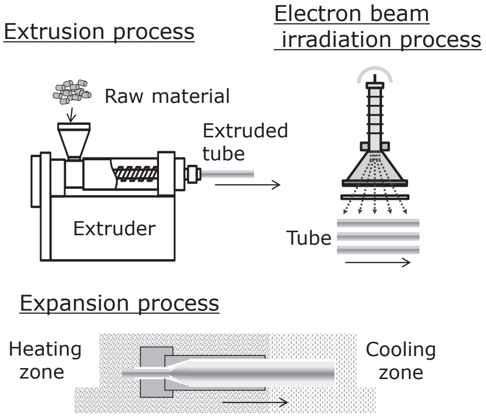

Fig. 2. Heat-shrinkable tubing manufacturing method

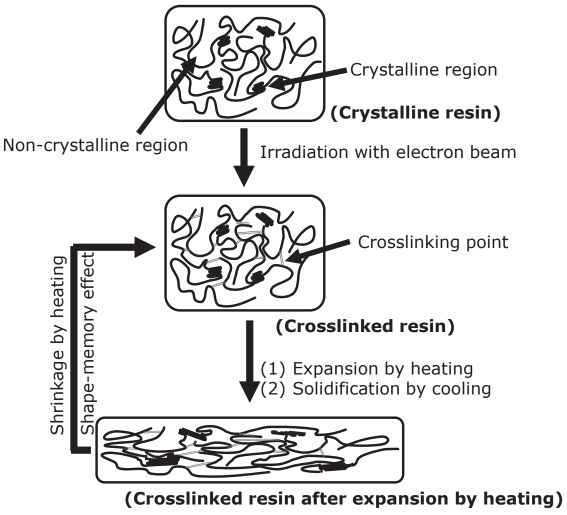

Fig. 3. Principle of developing heat-shrinkability

line and non-crystalline regions, the resin molecules are connected to each other in the non-crystalline region. As a result, the resin transforms into crosslinked resin with crosslinking points formed in the non-crystalline region. The crosslinked resin is expanded by heating, and then cooled and solidified as thermally expanded crosslinked resin. When the thermally expanded crosslinked resin is heated to a temperature equal to or higher than the melting point of the crystalline region, the crystal melts and becomes soft. As a result, due to the presence of the crosslinking points, the resin shrinks to the shape before expansion (shape-memory effect).(1)

### 3-2 Development of tubing material

The shrink temperature of heat-shrinkable tubing depends on the melting point of the resin used for the outer layer of tubing. From the viewpoints of cost, heat-shrinkability, and oil resistance, we selected polyethylene as a base resin. Polyethylene is economical and has excellent extrusion characteristics. As a result of the investigation of polyethylene, it was found that its coefficient of elasticity increases as its melting point increases as shown in Fig. 4.

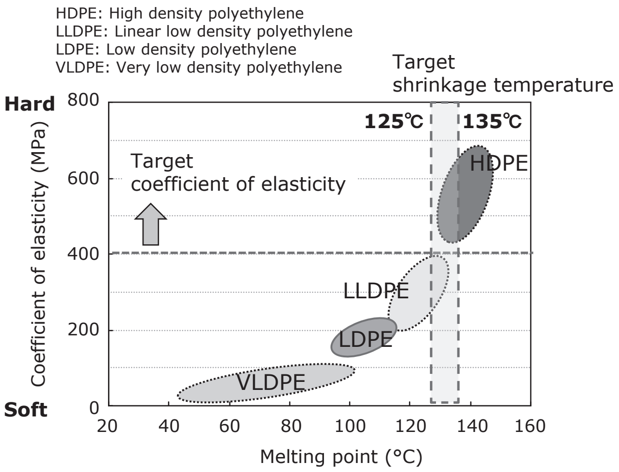

Fig. 4. Melting point and coefficient of elasticity of various types of polyethylene

High-density polyethylene (HDPE)*5 was expected to provide the tubing with high mechanical strength because its coefficient of elasticity is higher than those of other types of polyethylene. However, it was found that HDPE would not sufficiently shrink when heated to 135°C, a temperature slightly lower than its melting point, for one minute. In contrast, other types of polyethylene shrink when heated to 125°C but soften at a service temperature of 125°C, thereby producing internal stress in a radial direction and sliding out of its intended position (Fig. 5).

To eliminate these shortcomings, we blended a polymer into polyethylene to optimize its melting point. As a result, we developed a new polyethylene-based outer layer material. The new material shrinks when heated to 135° for one minute (percentage of heat shrinkage: 75% or more), but does not shrink at a service temperature of 125°C (percentage of heat shrinkage: 20% or less) or get out of position (Fig. 6).

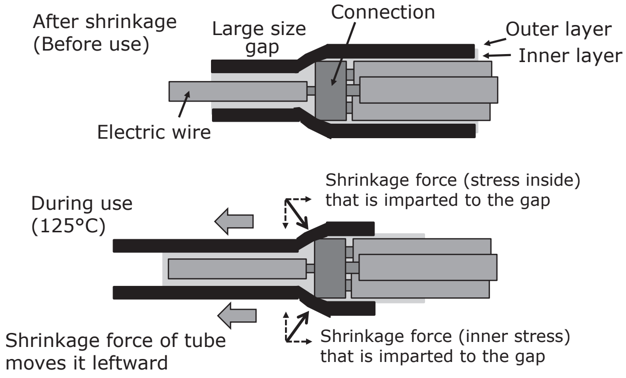

Fig. 5. Mechanism of positional displacement of tube when used

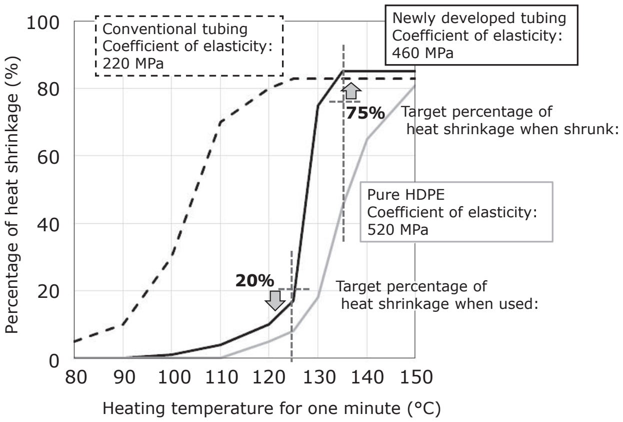

Fig. 6. Temperature-dependence of the coefficient of elasticity of newly developed tubing (outer layer)

## 4. Development of Inner Layer Material Having Optimal Composition

### 4-1 Inner layer material development

Polyamide resin was selected as the hot melt adhesive to be used for the inner layer since this resin provides a high degree of freedom of design and exhibits a wide variety of characteristics necessary for the inner layer. (1) The flow properties of the resin were optimized by molecular design. (2) The adhesion properties of the adhesive depends on the polarity of the material to which the adhesive is applied. Since polyamide resin itself does not adhere to polyethylene, the outer layer material (depending on its application, the tubing will be used to cover polyethylene wires), we introduced a polymer alloy technology to develop a new inner layer material.(2)

### 4-2 Target adhesive flow setting

To determine the target viscosity of the hot melt adhesive to be used for the inner layer, several types of dual-wall tubing were tested. For their outer layers, existing resin compound was used, while for their inner layers, various types of polyamide resin having different viscosities were used. After being shrunk by heating, each prototype tubing was removed from the covered object to check for conformance to the outer contour of the object and the flow properties of the adhesive in the usage environment. The results revealed that, when the tubing is shrunk by heating, an adhesive having a melt viscosity of 550 Pa･s or less conforms to the irregular outer contour of the object to be covered, and that an adhesive having a melt viscosity of 800 Pa･s or more does not flow out of the tubing. Based on the above results, we introduced molecular design technology to develop and use an inner layer material whose viscosity follows the curve shown in Fig. 7.

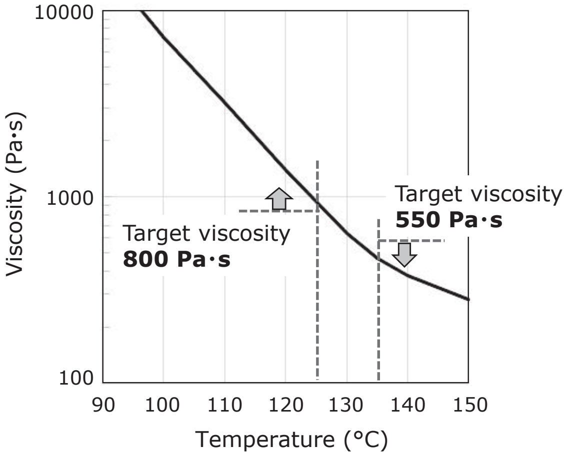

Fig. 7. Temperature dependence of the viscosity of newly developed tubing (Inner layer)

### 4-3 Development of material

Polyamide resin does not adhere to polyethylene. To modify this intrinsic property, we added a proper amount of olefin rubber to this resin. The structure of this rubber is similar to that of polyethylene. For polyamide resin with olefin rubber added, the adhesiveness of this resin to PVC and metals decreased as the composition of olefin rubber increased, and the adhesion to polyethylene did not significantly increase as expected (Fig. 8).

Subsequently, we tested a polymer alloy (Fig. 9) made by adding a small amount of olefin rubber to polyamide resin. In this test, the polymer provided the polyamide resin with a high adhesion to polyethylene while maintaining the high adhesion of the polymmide resin to PVC and metal. The results of the transmission electron microscopy of the phase structure (Fig.10) revealed that the olefin rubber dispersed finely on a nanometer order. We concluded that an increase in the adhesion of the polymer alloy was brought about by an increase in the interfacial strength between the polyamide resin and olefin rubber and an increase in the resistance to stress concentration.

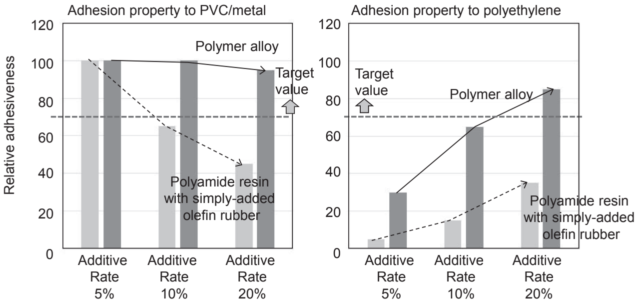

Fig. 8. Dependence of the adhesiveness of polyamide resin on the additive rate of olefin rubber (with the adhesiveness of conventionally used resin taken as 100)

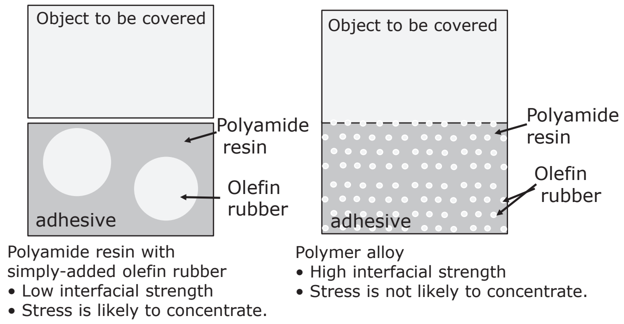

Fig. 9. Difference in adhesiveness between polyamide resin with simply-added olefin rubber and polymer alloy

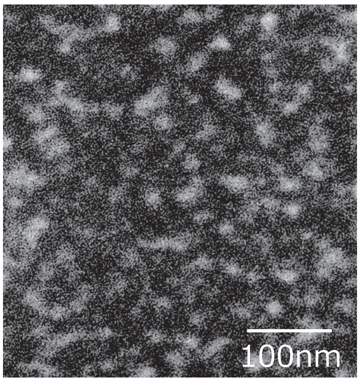

Fig. 10. Result of transmission electron microscopy of phase structure (Black: polyamide resin; white: olefin rubber)

## 5. Evaluation Result for Prototyped Dual-Wall Tubing

We prototyped a dual-wall tubing (before shrinking: inner diameter = 5.8 mm; inner layer wall thickness + outer layer wall thickness = 0.45 mm, after shrinking: inner diameter = 1.3 mm; inner layer wall thickness= 0.65 mm; outer layer wall thickness = 0.55 mm) consisting of the newly developed inner and outer layer materials. When shrunk to cover a one-to-three PVC wire connection using a tube shrinking machine, the prototype demonstrated sufficient waterproof and sealing performance. As a result of the observation of a cross section of the tube, it was confirmed that the hot-melt adhesive used for the inner layer had completely conformed to the irregular outer contour of the covered wire connection (Fig. 11).

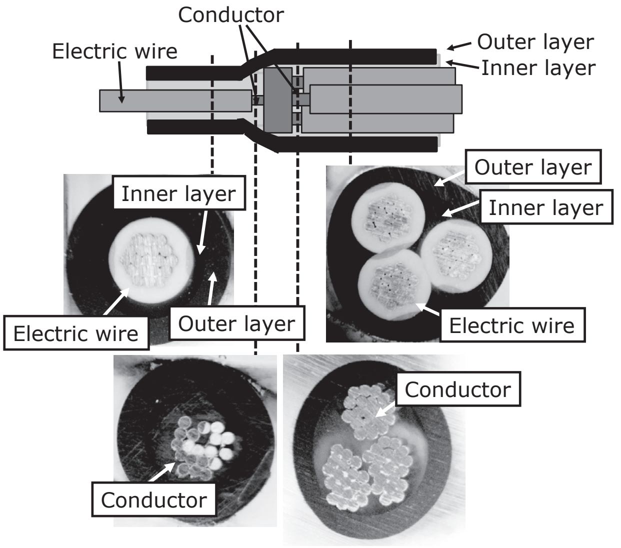

Fig. 11. Conformance of adhesive to irregular outer contour of wire connection

The physical characteristics of the prototype, which are shown Table 4, demonstrate that it achieves the target characteristics. Even after being heated to 125°C, the tube did not exhibit the outflow of the adhesive or positional displacement (Fig. 12).

Table 4. Evaluation results for newly developed tube

| Item | Condition | Target value | Result |
|---|---|---|---|
| Mechanical characteristics | Tensile strength | 10.4 MPa min. | 25 MPa |
| | Tensile elongation | 300% min. | 550% |
| | Coefficient of elasticity | 400 MPa | 460 MPa |
| | Piercing strength (V-shape blade/thrusting in) | 450 N min. | 520 N |
| | Thermal shock 225°C × 4 h | No crack generation | pass |
| | Heat resistance 130°C × 7 d | No crack generation | pass |
| Electrical characteristics | Dielectric strength | 15 kV/mm min. | 20 kV/mm |
| | Volume resistivity | $1.0 \times 10^{12}$ Ω•cm min. | $9.0 \times 10^{15}$ Ω•cm |
| Chemical characteristics | Flammability | SAE J1128 Self extinction of flame within 70s | pass |
| Sealing properties | Original | Leakage current 0.25 µA max. | pass |
| | 125°C × 1000 h after heat-aging | | pass |
| | Oil resistance Immersing in brake oil for 2 h | | pass |
| | Oil resistance Immersing in automatic transmission oil for 2 h | | pass |

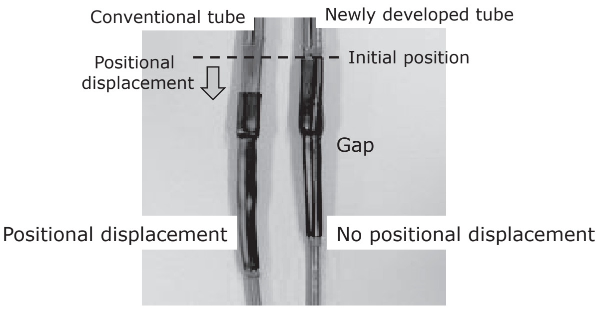

Fig. 12. Tube after being heated to 125°C
(Newly developed tube was free from positional displacement.)

## 6. Conclusion

We have developed dual-wall tubing that can be used to protect one-to-plural automotive wiring harness connections. When heated to a relatively low temperature (135°C), the new tubing conforms to the irregular outer contour of the wire connection. In addition, this tubing does not induce outflow of the adhesive or cause positional displacement, and demonstrates high mechanical characteristics under a usage environment of 125°C. Due to its excellent heat-shrinkability and sealing performance, the new tubing is expected to find wide applications in the automotive field.

- SUMITUBE is a trademark or registered trademark of Sumitomo Electric Industries, Ltd.

### Technical Terms

∗1 Polyvinyl chloride (PVC): A synthetic plastic polymer commonly used as an insulation covering for electric wires at service temperatures of approximately 80 to 100°C.

∗2 Percentage of heat shrinkage: The percentage calculated from 100 x (inner diameter before shrinkage – inner diameter after shrinkage) / inner diameter before shrinkage.

∗3 Electron beam: The flow of high energy electrons, which impinge against a substance to induce a chemical reaction by high electron energy.

∗4 Crystalline resin: Resin consisting of a crystalline region where molecular chains are arranged in an orderly way and a non-crystalline (amorphous) region where molecular chains are arranged randomly.

∗5 High-density polyethylene (HDPE): A highly crystalline polyethylene in which repeat units of moderate/low pressure-polymerized ethylene are linked linearly with little branching.

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